A STUDY OF THE EFFECT OF PRESSURE ON THE VISIBLE SPECTRUM OF OZONE

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A STUDY OF THE EFFECT OF PRESSURE ON THE VISIBLE SPECTRUM OF OZONE

I SUMMARY

The absorption spectrum of ozone in the visible region consists of a number of rather diffuse maxima which under ordinary conditions exhibit no fine structure. These bands have been found to exhibit a pronounced pressure or solvent sensitivity at high pressures of admixed gas or solvent.

This region of the spectrum has heretofore been investigated only by use of rather dilute mixtures of ozone in oxygen, and the several investigators have obtained results which in some respects vary quite considerably.

The present work, therefore, was done to accomplish three separate purposes. First, by working with pure ozone, any perturbing influence of foreign gas was removed, and an accurate graph of the molar extinction coefficients of ozone in the visible region was obtained to replace the rather questionable ones derived from work done on dilute mixtures.

Second, the possibility that under favorable conditions of low pressure and long optical path the maxima in the visible region might be resolved into fime structure was investigated, working with a 17 meter cell and at one millimeter pressure. No fine structure was observable under these conditions.

Third, the effect on the absorption spectrum caused by the addition of varying low pressures of various gases was studied, and an attempt was made to correlate the results with the pressure effect at high pressures. As compressing gases, oxygen, argon, nitrogen, carbon dioxide, water vapor, carbon tetrachloride vapor and ozone itself were used.

The effect caused by foreign gases was found to be a combination of at least two factors: a pressure effect and a dipole force-field effect. The pressure effect was found in measurements with gases which, because of symmetry, could have no dipole or quadrupole moment, and hence no force-field. The force-field effect was found only in those measurements in which the foreign gas had a dipole or quadrupole moment. In these measurements both force-field and pressure effects appeared.

In general, the effect of the foreign gas on the spectrum of ozone was found to be least at about 6000 Angstroms, increasing at increasing distance from this region.

II INTRODUCTION

Although there has been extensive work done on the absorption spectrum of ozone, most of it has been done in the ultraviolet and infra-red, and that which has been done in the visible has been done using mixtures which were of relatively low ozone content with oxygen always as the diluent gas. Possibly as a result of this there has been a considerable lack of accord in the conclusions arrived at by the various workers. Also, it has been found that the shape of the absorption spectrum is dependent on the pressure of foreign gas present in the absorbing cell. For these reasons, it was thought desirable to make a series of measurements on the spectrum of pure ozone at varying pressures and using various foreign gases as compressing agents, to see whether use of the pure gas might not cause at least some of the difficulties and discrepancies observed in work with the diluted gas to disappear.

The objects of this work were threefold. First, it was desired to investigate the possibility that under suitable conditions of long absorbing path lengths, low pressure, and pure ozone, the maxima which have been observed to occur at 5710 and 6070 Angstroms in the visible absorption spectrum might exhibit fine structure resolvable by instruments of medium dispersing power. From this fine structure, if found, would be calculated further information regarding the physical structure of the ozone molecule, to supplement that obtained from measurements in the infra-red and ultraviolet.

Second, as has been mentioned, the absorption spectrum in the visible has been found to be pressure sensitive. In work conducted here, Robinson has found that the molar absorption of pure ozone in solution

using various solvents is larger than that of the pure gas at comparable partial pressures, and he has offered an explanation for this effect. Since the ozone solution corresponds to ozone in an extremely high pressure of foreign gas, this effect suggested that the difficulties encountered in work with mixtures of ozone in other gases might at least in part be explained on the basis of this pressure sensitivity. To complement this work at high pressures it was desired to measure the effect on the absorption spectrum of pure ozone of pressures ranging from zero to several atmospheres, using various other gases as compressing agents. It was thought that by this means the dependence of the absorption coefficients of ozone on pressure of external gas might be found as a function of pressure over the pressure range zero to approximately 200-250 atmospheres pressure of foreign gas. From this pressure dependency it was hoped that conclusions might be drawn regarding the structure of the ozone molecule in the ground state, excited states, and possible transition mechanisms.

Third, since there is still disagreement as to the actual shape of the absorption curve of ozone in the visible region, it was hoped that by use of pure ozone with no compressant present, and careful measurements of extinction coefficients, a reliable graph of the extinction coefficient curve which would be correct in contour as well as in magnitude might be obtained.

III LITERATURE SURVEY

A considerable amount of work has been done on the absorption spectrum of ozone, in the infra-red, visible, and the ultraviolet regions, as well as a small amount of recent work with electron diffraction techniques. The ultraviolet has been most extensively surveyed, possibly because of its importance in reference to atmospheric studies, and also because of the greater absorption coefficients of ozone in this region as compared to the visible and infra-red. Ozone in the ultraviolet exhibits well defined vibrational fine structure and sharp, clean band systems, whereas in the visible region the bands are quite diffuse and hazy.

The bands in the ultraviolet have been well tabulated and ordered by several workers. Ny and Choong[1] have measured the extinction coefficients for ozone mixtures in the range 2000-3400 Angstroms, using a high dispersion quartz spectrograph and photometric techniques. Vassy,[2] Lefebvre,[3] Barbier and Chalonge,[4] and others also have determined ex-

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[1] T. Ny and S. Choong, "L'Absorption de la Lumiere par Ozone entre 3050 et 3400 Angstroms (Region des Bandes de Huggins)," Comptes Rendus des Seances de l'Academie des Sciences, 195: 309, (1932)

[2] E. Vassy, "Influence de la Temperature sur le Spectre d'Absorption de l'Ozone," Comptes Rendus des Seances de l'Academie des Sciences, 202: 1426, (1936)

[3] L. Lefebvre, "Sur le Depression de Certaines Bandes du Spectre de l'Ozone sous l'Action du Froid," Comptes Rendus des Seances de l'Academie des Sciences, 199: 456, (1935)

[4] D. Barbier and D. Chalonge, "Sur les Coefficients d'Absorption de l'Ozone dans la Region des Bandes de Huggins," Annales de Physique, 17: 272, (1942)

tinction coefficients in this region in the course of other work with pressure and temperature sensitivity of the spectrum, without attempting extensive theoretical analyses of their findings.

The infra-red band systems of ozone have been tabulated by various workers, and theoretical analyses of their results have been attempted, with not the highest order of agreement. Adel and Dennison[5] have analyzed the fine structures of the 14.6 mu band and on their conclusions base a proposal of an acute isosceles triangle as a model for the ozone molecule. They give the apical angle as 34°, base bond length as 1 Angstrom and sides as 1.69 Angstroms.

Shand and Spurr[6] on the basis of electron diffraction measurements, propose an obtuse model with apical angle 127° and side bonds 1.26 Angstroms, which would require an extremely long 2.25 Angstroms base bond.

Glockler and Matlack[7] suggest that an acute triangle with apical angle 52°, 1.45 Angstroms base and 1.21 Angstroms sides best fits the bond energy and infra-red requirements as deduced from thermodynamic considerations.

On the basis of a bond energy versus bond distance chart for

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[5] A. Adel and D. Dennison, "Notes on the Infra-red Spectrum and Molecular Structure of Ozone," Journal of Chemical Physics, 14: 379, (1946)

[6] W. Shand and R. Spurr, "The Molecular Structure of Ozone," Journal of the American Chemical Society, 65: 179, (1943)

[7] G. Glockler and G. Matlack, "The Force Constants of Ozone," Journal of Chemical Physics, 14: 531, (1946)

the oxygen bonds. Eberhardt[8] proposes an obtuse triangle with apical angle of 100° and sides 1.27 Angstroms.

The work in visible regions, although begun at an earlier date, is somewhat less extensive than in the other two regions. Chappuis[9] in 1880 observed that the visible absorption spectrum of ozone exhibited a series of diffuse maxima, which disappeared on heating. In 1906, Ladenberg and Lehmann[10] tabulated the bands in the visible region. Colange[11] in 1927 measured the extinction coefficients of ozone in dilute ozone-oxygen mixtures. In the period following 1937 Vassy[12] and others have published a series of papers on extinction coefficients for such mixtures, which in general are directed toward atmospheric studies. In 1947 Humphrey and Badger[13] published a series of measurements on the visible spectrum, done at high dispersion, to measure temperature sensitivity of the spectrum and also to examine it for possible fine structure. In common with all reported earlier work, they employed

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[8] W. Eberhardt, Private Communication

[9] J. Chappuis, "Sur le Spectre l'Absorption de l'Ozone," Comptes Rendus des Seances de l'Academie des Sciences, 91: 985, (1880)

[10] E. Ladenberg and Lehmann,"Uber Versuche mit Hochprozentigem Ozon," Annalen der Physik, (4) 21: 305, (1906)

[11] M. Colange, "Etude de l'Absorption par l'Ozone dans le Spectre Visible," Journal de Physique et la Radium, (6) 8: 254, (1927)

[12] A. Vassy, "Coefficients d'Absorption de l'Ozone dans la Region des Bandes de Chappuis," Comptes Rendus des Seances de l'Academie des Sciences , 206: 1638, (1938)

[13] G. Humphrey and R. Badger, "Absorption Spectrum of Ozone" Journal of Chemical Physics,15: 794, (1946)

a rather dilute mixture of ozone and oxygen.

The results of these various measurements are in general not too concordant. The major absorption peaks at 5770 and 6010 Angstroms are well agreed upon, but minor maxima are reported variously as present or absent. For instance, Colange described a series of small maxima at 4650, 4750, 4800, 4900, 5050, 5150, 5350, 5450, 5700, 6010, and 6250 Angstroms. Of these, Vassy reports only the major maxima at 5050, 5350, 5700 and 6010 Angstroms, the others not appearing. Robinson also reports only these maxima. Graphs of these results are shown in Appendix IV. It seems probable that at least a majority of the minor maxima reported by Colange are actually present, and were missed by the other workers as a result of taking points too widely separated through which to draw their curves. There is also the possibility that these maxima, due to their extreme weakness, were physically masked by the stronger maxima in the cases where photographic densitometry was employed to find extinction coefficients.

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[14] G. Robinson, Thesis, Georgia Institute of Technology (1949)

IV APPARATUS

In general, the apparatus for preparation and purification of liquid ozone is similar to that employed by Wulf and Karrer[1] but with minor modifications. The train consisted of a safety trap to prevent back pressure forcing sulfuric acid into the oxygen reducer valve, a sulfuric acid bubble column and a P_2O_5 drying tube to remove any water vapor, a fritted glass filter to remove dust, the ozonizer itself, a refrigerated trap for oxides of nitrogen, the condensing cell, and connections to vacuum pump. This train is shown in Figures 1 and 2. Of the component parts, the drying section and fritted filter are standard design. The ozonizer, however, is a new and highly efficient modification of the customary Siemens type ozonizer, the point of interest being that in place of silvered or tinfoil electrodes the inner finger is filled with water, and water circulates through a sealed-on outer jacket, electrical connections being made to these volumes of water. The outer circulating water serves also to cool the ozonizer and increase its efficiency.

A high voltage X-ray transformer whose primary voltage is controlled through an autotransformer is used as a source of potential, the ground side being connected to the outer jacket and grounded to the water pipes. The nitrogen oxides trap consists of a helix of glass tubing immersed in a Dewar flask of dry ice-methanol freezing mixture. Since any nitrogen present in the ozonized gas is immediately and

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[1] E. Wulf and R. Karrer, "Preparation of Pure Ozone and Determin- of its Molecular Weight," Journal of the American Chemical Society, 44: 2391, (1922)

quantitatively oxidized to nitrogen pentoxide, and at the temperature provided by the freezing bath nitrogen pentoxide is a solid with a vapor pressure of about .01 millimeters, this is a sufficient trap.

The condensing cell, shown in Figure 2, consists of a 25 milliliter Erlenmeyer flask with the neck lengthened and connected with inlet and outlet tubes as shown. This cell was mounted so that a Dewar flask of liquid nitrogen could readily be placed in position to cool the cell. Since liquid ozone is a fairly shock-sensitive high explosive, provision was made to adjust the coolant level mechanically. The Dewar flask was carried on a small elevator mechanism which consisted of a flat plate secured to a nut which traveled on a vertical lead screw, but was prevented from rotation by a vertical detent. As the lead screw was driven in either direction by a small reversible electric motor, the platform was driven either up or down, adjusting the level of coolant relative to the condensing cell. A 145 RPM motor was used, which made the total transit time from top to bottom about 15 seconds, permitting fairly fine adjustment of the level of liquid nitrogen and hence good control of the fractionation process. The entrance and exit tubes of the condensing cell were connected to explosion traps to protect the rest of the apparatus in case of ozone explosions. These traps consisted of sections of large bore tubing on which were blown bulbs which were allowed to cool rapidly, creating strains. These bulb-tubes were connected to the rest of the ozonizing train through short lengths of capillary tubing. The capillary sections allowed the gas to flow as long as the flow was normal, but gave an effectively solid barrier to the shock wave of explosion, while the strain-weakened bulb-tubes shattered easily to relieve the

pressure. In actual practice this device worked exactly as anticipated, confining several explosions to the actual condensing cell. The entire assembly of elevator, condensing cell, and explosion traps was shielded by a pane of armor glass hingeg to a frame which contained the condensing assembly. The debris from an explosion was thus prevented from flying about and doing possible further damage. The complete ozonizing and purifying train is shown in Plates I and II.

Three optical cells were used during the course of the research. The first was a tube of 12 millimeter glass, 117 centimeters long, with optical glass windows sealed on the ends, and provided with a manifold to allow evacuation of the cell and entry of metered amounts of ozone and other gases, with decomposers to protect the manometer and vacuum pump. The decomposers consisted of tubes of granular soda lime heated by electric windings and covered with asbestos paper. The temperature was controlled by controlling the heater current through a Variac. The manometer used was a simple vacuum U tube mercury manometer reading to slightly over one atmosphere. With care this manometer could be read to .5 millimeters. The manifold was made of 5 millimeter tubing. Silicone stopcock grease was used on all stopcocks, and was found to be satisfactory so long as no heat was nearby, and so long as the old grease was thoroughly cleaned off before new grease was applied.

The second cell employed was constructed of 12 millimeter tubing, with cell windows attached by means of ground glass joints. The cell was originally in the form of a U, of about 17 meter leg length. It was proposed to send light down one leg of the U, reflect it around the U and out the other leg into the spectrograph. At first it was pro-

posed to do this by silvering the U and adjacent straight portions, but light losses were prohibitive. A set of windows and a connecting tube being put in place of the U, an attempt was made to reflect the light back by mirrors. When this also failed, the light source was placed in back of the return half of the cell and only this half was actively used. The manifold and decomposers for this cell were essentially the same as those for the first cell, except that in this case the manifold had somewhat more volume than the cell, since the idle half of the cell was incorporated in the manifold. This was found to be a serious drawback to the use of this cell. The entire cell was cased in aluminum conduit which rested inside copper tubing, which in turn was hung from bench supports. The tube was hung in slings which were adjustable laterally and vertically for truing up the cell. The glass was inserted and sealed together from four foot lengths, and tested for leaks at each seal as it was made. The cell could maintain a vacuum of less than one millimeter for over a week when in proper operating condition.

The third cell was made of a section of 22 millimeter tubing 121 centimeters long, with optical windows sealed on the ends. Certain changes were made in the manifold from that of the first cell to eliminate a difficulty which arose during entry of compressing gas, namely a change in amount of ozone in the optical path. Also, a heated capillary spiral was substituted for the soda lime tube in the manometer decomposer to prevent possible dispersion of soda lime dust throughout the cell and manifold as a result of sudden surges of gas through the decomposer. The spiral was heated by electric windings as was the soda lime tube.

Both short cells were mounted behind a safety shield on an optical bench made of 6 inch C beam slotted accurately. On the third cell, provision was made for cooling the cell with dry ice by building a trough around the cell and closing the ends of the trough with blocks through which the ends of the cell extended.

The first analytical instrument used was a Cenco grating spectograph of 109 centimeters focal length, dispersion 15.9 Angstroms per millimeter, employing a replica reflection grating. As constructed, the instrument required 2¼ by 11 inch plates, which were unavailable. Consequently, the plateholder was altered to use 35 millimeter spectographic film. The machine was mounted and focussed, and aligned by use of an iron arc and later a mercury arc lamp, which was used as a standard. Nine exposures could be made on each strip of film, using an aperture of 1.5 millimeters on the film mask. An electrical timing shutter was constructed for the spectrograph so that all exposures should be for the same time. The slit mechanism of the spectrograph was covered by an aluminum plate which had a hole in it placed just to allow light to pass thru it and strike the slit. This hole was ordinarily covered by a light aluminum plate, but during an exposure, the plate was moved aside by an actuator mechanism. This was constructed by removing the contacts from a heavy relay and using the coils and rocker as activator for the shutter itself thru a lever arrangement. The exposure time was thus the same as the time of energizing of the relay coil. A constant speed gear train driving a cam which was followed by a micro-switch provided the timer. It was found that with this mechanism, exposures were reproducible in

time to the limit of stopwatch accuracy. The exposure time used was 31.6 seconds.

A mercury arc was used as standard of wavelength on the first cell, an iron arc was used for cells two and three. These were mounted to one side of the spectrograph and their light directed into the slit by a mirror. As light source, with the first cell a microscope lamp using a 100 watt frosted incandescent bulb was used. With cell two, a 1000 watt projection bulb run at 95 volts was used with a concave reflector. With the third cell, a 100 watt projection bulb was used in a microscope lamp housing, focussed by means of a quartz lens. These lamps were mounted in place rigidly with respect to the cell.

In order to evaluate the films obtained by use of the spectrograph, it was necessary to construct a microphotometer. A view of the completed instrument is given in Plate IV. The machine consists of a mechanical film carrier, an optical assembly, an amplifier and a recorder. The film carrier consists of a steel box base with one precision ground vee track and one precision ground flat track. On these tracks ride a three wheel carriage, the two front wheels being shaped so as to engage the vee track and keep the carriage in rigid alignment. Provision was made by means of a dovetailed cross-slide controlled by a feed screw for traversing the film laterally across the field of view. A slot one inch by ten inches cut in the carriage allowed exposure of the entire film to the optical path. Longitudinal motion of the carriage was obtained by means of a metric lead screw, through a detachable clutch. The lead screw had a hand wheel graduated in 10 micron units,

and was driven thru a series of reduction gears by a small constant-speed motor. By suitable interchange of gears in the gear train, speeds varying from 4 millimeters per hour to 60 millimeters per hour were obtainable for the carriage.

At the rear of the base was attached a pedestal to which was secured the optical tube of a comparator microscope. A six volt light bulb, powered thru a Variac, in a housing at the rear of the pedestal was arranged to send light thru a shutter aperture in the pedestal onto a mirror which reflected it up thru a condenser lens onto the film. The condenser lens was adjustable for focus by means of a vertical track dovetailed to the rear rail, which supported the condenser mount, and a drive screw geared to a knob on the front of the base. The eyepiece was removed from the microscope and a 45° mirror arranged to reflect the light onto an adjustable slit behind which was a vacuum photoemissive cell in an otherwise light-tight housing. The output of this cell was amplified by a D C amplifier and sent to the recorder, which was a Brown Electronik recording potentiometer. The power source for these electric instruments was a Sola constant-voltage transformer. An automatic marking device was incorporated in the microphotometer, to furnish a reliable distance scale on the recorder chart to correspond to a distance scale on the microphotometer carriage and thus enable easy and rapid determination of a wavelength scale on the chart from the fiducial exposure on the film. This marking device was a long period relaxation oscillator, charging a four microfarad capacitor thru a variable 100 megohm resistor, to the firing voltage of a neon lamp. A micro-switch

actuated by a depression on the lead screw of the microphotometer kept the firing circuit open except for a moment during each revolution as the zero on the hand wheel was reached. When sufficient charge was stored to fire the tube, the current which flowed entered the amplifier of the microphotometer as a blip of electricity which sufficed to cause the recorder pen to make a very rapid excursion away from and back to its point of balance, making a fine pointed "tooth" on the trace. Since this could only come at an integral number of revolutions of the lead screw, and was adjustable to some extent by varying the resistance in the oscillator, it was possible to have a completely trustworthy scale automatically recorded directly on the chart being made.

After much careful effort had been expended, it was decided that the spectrograph was not suitable for the work at hand, for a reason given in Appendix I. Hence a Beckman DU quartz spectrophotometer was employed for the remainder of the work, both as a non-recording instrument and after alteration to make it recording. The changes and additions necessary to make it recording are described in Appendix VI.

V EXPERIMENTAL TECHNIQUE

To prepare ozone, it was necessary only to fill the nitrogen trap with dry ice-methanol mixture, place a Dewar flask of liquid nitrogen around the condensing cell, turn on the circulating water in the ozonizer, turn on the oxygen valves, and switch on the high voltage transformer. The rate of flow of the oxygen through the ozonizer seemed to be fairly independent of the concentration of ozone produced, so that a fairly rapid bubbling, rapid enough to cause froth in the sulfuric acid tube, still yielded a mixture high in ozone content. Although a quantitative analysis of the mixture formed by this apparatus has not been performed, rough calculations on vapor pressure and times observed give values ranging up to 12 per cent. It was only necessary to be sure to maintain the liquid nitrogen level at about the bottom of the conical section of the Erlenmeyer flask to get immediate and abundant condensation of dark blue liquid ozone, with very little of the lighter blue liquid oxygen in evidence.

After sufficient ozone for the purpose at hand had been generated, which took about two hours, the ozonizer was turned off, a stopcock between the nitrogen trap and the condensing cell closed, the cell immersed well into the liquid nitrogen and vacuum applied to fractionate off the liquid oxygen at the temperature of liquid nitrogen. At this temperature, ozone has a vapor pressure of only .01 millimeters, oxygen a vapor pressure of 162 millimeters, and nitrogen of course, a vapor pressure of 760 millimeters. Since oxygen and ozone form a two phase

system, one of ozone in oxygen and one of oxygen in ozone, and the ozone in oxygen phase is lighter, it was easy to distil off essentially all of the oxygen, leaving pure liquid ozone behind. The completion of the removal of oxygen was signaled by a sudden and rapid drop of the pressure from about 16 centimeters to practically zero. When this drop was reached, a few minutes pumping to remove gaseous oxygen completed the purification. The pump could then be turned off, and as long as the ozone cell was kept well immersed in liquid nitrogen the vacuum maintained itself, showing the slow rate of decomposition at this low temperature and the relative purity of the ozone as regards the other permanent gases.

Liquid ozone, even more than ozone gas, is a shock sensitive high explosive with a very low activation energy. It liberates 34.6 kilocalories per mole on decomposition. Since so little shock is necessary to detonate it as to make it often seem to decompose spontaneously, the problem of how to regasify the pure ozone was a serious one. Indeed, several cells were lost by such explosions, along with the Dewar flasks, and the worth of the safety shield and the explosion traps was amply demonstrated. The armor glass was heavily pitted and cracked by the explosions, none of which concerned as much as a half milliliter of liquid ozone.

An apparently satisfactory answer to the problem was found by accident. The silicone stopcock grease employed was attacked by the ozone and oxidized to a fluffy white silica gel. Some of this was swept accidentally into the condensing cell by the gas stream. This gel

seems to act as an inhibitor for the decomposition, probably by offering an adsorbing surface from which the ozone may fume off without ever being present in bulk liquid form. This cell was subjected to relatively rigorous tests to determine the protective power of this gel. Liquid ozone was allowed to warm to room temperature both under vacuum and at normal pressure, without any untoward effect. That it is not a complete answer is evidenced by the fact that under extreme conditions of temperature change the cell was finally destroyed, but in comparison to the unprotected cell, the one containing silica was much less sensitive to handling.

After all the oxygen had been removed from the condensing cell by fractionation, on lowering of the liquid nitrogen flask so the condenser bulb stood free in the cold air column inside the Dewar flask, the ozone would gradually warm up and fume off. It could then be led into the previously evacuated optical cell by having open the connecting stopcock. When sufficient ozone pressure had been reached in the optical cell, closing of the stopcock and reimmersion of the condenser in the liquid nitrogen recondensed the excess ozone and stored it for further use.

In general, the various exposures were made in the same way. The pressures of gases in the optical cell being arranged by letting in appropriate amounts of each, the lamp was turned on and the film exposed for a standard time through a standard slit. With the short cells, 30 seconds was found sufficient; with the long cell, exposures up to two hours were necessary in some cases. A fiducial exposure of the iron or mercury arc was made first, then up to eight of the ozone cell on a

single strip of film.

Development was as near ly reproducible as possible. The film was developed six minutes in fresh D-19 developer, washed one minute, fixed four minutes, then washed and dried, after which it was mounted in the densitometer frame to set to size. Slight deviations in size were noted from film to film, but these deviations were taken into account automatically when the wavelength scale was applied.

Several experimental difficulties arose in connection with the photographic technique which made it necessary to turn finally to a different technique. First, the spectrograph employed used a replica grating which introduced an interference phenomenon into the dispersed spectrum. This interference, which is discussed more fully in Appendix I, was of sufficient strength as to mask the relatively weak band structure due to the ozone absorption completely. An exposure sufficiently short to leave the interference structure resolved was too short to record the weaker ozone bands while one long enough to record the ozone bands would be completely burned out by the stronger interference bands. Also, because of the spillage of some mercury from a broken manometer, the films used were sensitized and prefogged an uncertain amount, although the film was stored in a separate room. This was in some cases sufficiently serious as to make the exposure of no use for quantitative work.

To remove some of these sources of error, various methods were tried. As summarized in Appendix II, a mask was made to mount in the spectrograph to suppress the interference bands. This was only partly successful, since the mask was at best accurate for only one fixed

exposure time and slight deviations were sufficient to reintroduce false band structure. Also, the light passing through the mask was to some extent diffused, thus broadening and weakening the already broad and weak ozone bands.

Photometry of the films was done on the instrument described in the section on equipment, a graph of the intensity of light transmitted by the film being obtained. To interpret these graphs, it was necessary to calibrate the sensitivity of the film at various wavelengths as a function of wavelength and light intensity. This was done by preparing a series of neutral filters of known percent transmission, making a series of exposures through these filters and graphing the relationship between the logarithm of the percent transmission of the neutral filter against the measured density of the film. Such graphs were made at 100 Angstrom intervals from 4500 to 6700 Angstroms. From these graphs, by putting in values for density of a film at the given wavelengths, one could obtain values for the density of the filter medium, which in our case would be ozone, at the same wavelengths. From these values of optical density of ozone, knowing the pressure in atmospheres of ozone present in the cell at the time of exposure and the length of the cell in centimeters, it was immediately possible to obtain values for the molar extinction coefficients of ozone at these wavelengths and construct a graph of them over the region measured.

In spite of the considerable effort and time expended in trying to eliminate the various difficulties attendant upon this photographic method of measuring extinction coefficients, we were finally forced to

conclude that the difficulties and uncertainties involved were too great to allow reliable measurements to be made with the equipment at hand and in the time available. Consequently we were obliged to abandon this method and finish the investigation by use of a spectrophotometer. This instrument is described in Appendix VI.

In using the recording spectrophotometer with which the work was finally completed, the machine was stabilized on dark current so that the dark current curve would fall on a convenient low range, and the intensity of the light source adjusted by means of the slit to make the I_o curve lie on the higher end of the range. Then after running a trace on the empty cell to obtain an I_o curve, the ozone was allowed to enter the cell in the regular way, and a trace of I_{ozone} was immediately run.

These traces were converted into extinction coefficient graphs in the following way. The span from dark current curve to trace was measured on an exponential scale, the readings of I were subtracted from the corresponding I_o readings to give optical density, from which, by Beer's Law, the extinction coefficients were obtainable, knowing the path length and the pressure of ozone.

The region at 3300 Angstroms was used as a relatively temperature and pressure insensitive standard from which to calibrate a density versus pressure curve for ozone. Using this curve and taking a reading at 3300 Angstroms for each run in the visible region, it was possible to correct graphically for decomposition of the ozone.

VI RESULTS AND DISCUSSION

The following results were obtained for the three objectives of this research, with the interpretations given below.

Fine Structure Search. Although Humphrey and Badger[1] in their work on the visible spectrum of ozone had searched for fine structure and found none, it was thought that possibly their failure to find any was due to unfavorable experimental conditions in which the fine structure was obscured by broadening due to Lorentz pressure effect and possibly also to the foreign gas present which might exert a force-field or Stark effect broadening. It was thought that possibly by working with pure ozone at sufficiently low pressure to remove the pressure broadening and any possible perturbation due to foreign molecules, and a sufficiently long optical path to provide sensible absorption, a careful survey might reveal rotational fine structure in the visible region, particularly in the strong maxima at 5770 and 6010 Angstroms and longer wavelengths, with a possibility of its occurence also at the short wavelength end of the region, around 4800 Angstroms. There was little chance of there being any fine structure in the intermediate wavelengths, due to pre-dissociation.

Ozone may be considered to decompose primarily into an oxygen molecule and an oxygen atom, as shown in Table I of Appendix IV, with the configuration of the decomposition products depending on the energy

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[1] G. Humphrey and R. Badger, "Absorption Spectrum of Ozone in the Visible," Journal of Chemical Physics, 15: 794, (1947)

of dissociation. Consideration of thermochemical data gives the energies corresponding to the three lowest-lying decompositions as being respectively 11917 Angstroms, 6166 Angstroms and 4677 Angstroms.

If the ozone molecule is excited to a potential energy curve which is as high as one of these dissociation energies and if there is a second curve which approaches the dissociation energy as a limit at high internuclear distances, then if the two excited level curves cross, according to the Franck-Condon principle, predissociation may occur. If the vibrational energy of the molecule is so low as not to reach the crossing point there will be no predissociation and if there is sufficient vibrational energy to make the molecule pass the crossing very rapidly there may not be time for the rearrangement necessary for the molecule to enter the dissociation curve and again there will be no predissociation. If, however, the molecule spends an appreciable amount of time at the crossing, chances for the necessary rearrangement are increased and predissociation will probably occur. If predissociation occurs, generally it takes place before the molecule can complete a rotation in the upper energy state, so the rotational energy is not quantized, hence no rotational fine structure can appear. Hence, if in our case the ozone molecule is excited with light of sufficient energy to just exceed the 6166 Angstrom dissociation level, chances for predissociation are good. If on the other hand light of considerably more energy excites it, it might not predissociate fast enough to prevent leaving rotational fine structure.

There was therefore the possibility that in the region around

4800 Angstroms there would be rotational fine structure due to high vibrational levels in the 6166 Angstroms electronic band with not quite enough energy to decompose by the 4677 Angstroms route. At wavelengths longer than 6166 Angstroms, rotational structure would be due to molecules with insufficient energy to reach the predissociation crossing. As a comparative example of predissociation one could consider the sulfur dioxide molecule. At about 2800-2600 Angstroms an apparent predissociation effect occurs in the band system. This has been shown by Franck, Sponer and Teller[2] to be a spurious predissociation, actually caused by an abnormally large pressure broadening which becomes serious above 2.5 millimeters. At 1950 Angstroms appears the first true predissociation, which corresponds to the dissociation of the molecule into SO and O. It was on the basis of this type of spurious predissociation that it was hoped the ozone spectrum would develop fine structure at low pressure.

In order to test the equipment for resolving ability for fine structure such as ozone was expected to exhibit, a measurement was made on the fine structure in the red bands of NO_2. This molecule was chosen as being very similar in weight and structure to the ozone molecule. The apical angle in NO_2 is 120°, compared to $100\text{-}127^\circ$ for ozone, and the bonds are 1.15 Angstroms, compared to 1.2-1.27 Angstroms for ozone. The molecular weight is 46, compared to 48 for ozone. Therefore its

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[2] H. Sponer, Molekulspektren, Ann Arbor: Edwards Brothers, 1945

vibrational and rotational spacings should be very similar in size to those of ozone. Upon examination of the exposure it was found that the average space between lines was of the order of 2 to 3 Angstroms, and the closest measureable doublet was about .9 Angstroms, in the region 6000-7000 Angstroms.

The limit of resolution for the spectrograph was somewhat below this. Using a grating of about 3/4 inch length and 15,000 lines per inch, the resolution was easily calculated

$$\lambda/\Delta\lambda = nN$$

where λ is the wavelength, $\Delta\lambda$ the resolvable difference in wavelength, n the order of spectrum used and N the number of usable lines on the grating. For λ the region at 6000 Angstroms,

$$6000/\Delta\lambda = 1 \cdot 3/4 \cdot 15{,}000$$

$$\Delta\lambda = .5 \text{ Angstrom}$$

This value was checked experimentally by measuring close doublets in the iron arc. It was found that lines .6 Angstrom apart were clearly resolvable visually. To test the resolving power of the densitometer, the somewhat less intense lines in the NO_2 spectrum were photometered. At low speed of the driving mechanism the fine structure was clearly resolved.

Using an optical cell of approximately 17 meters length and working at pressures of about one millimeter, working with pure ozone, a series of exposures were made and examined for possible fine structure. None was found and no appreciable change in shape or intensity

of the spectrum from that at relatively high pressures was observable.

These measurements, however, were subject to certain possible errors. First, the pressure was measured with a mercury manometer, shielded of course by a decomposer. With this arrangement an error of .5 millimeter was not impossible. Since the pressure effect was expected to obscure the fine structure down to a pressure of about this magnitude it is possible that through some systematic error the pressure was actually on the borderline of the pressure damping and that further reduction of pressure would have revealed fine structure.

Second, the cell employed was of small bore tubing and internal reflections were high, reducing the light intensity to such a degree that exposure times of hours were necessary to secure sufficient darkening of the film, using the narrow slit necessary to resolve the fine structure. In this lapse of time a significant amount of the ozone initially present could have decomposed unnoticed since there was no perceptible color to the emergent light. Also in the time of the exposure any extraneous light which leaked into the spectrograph could raise the fog level to such an extent as to greatly destroy the contrast between the lines and the spacings.

Third, the film employed was of rather coarse grain size, so that for the somewhat faint exposures obtained, the individual grains being somewhat separated precluded the use of the extremely narrow densitometer slit which was desirable for photometry of these films. With a narrow slit, statistically there were so few grains between light and slit that the passage of the individual grains across the slit was

sufficient to introduce a false fine structure appearance. Due to the necessarily wider slit used to decrease this effect, it is possible that fine structure actually present but very faint would not appear because of the slight change in average film density as a narrow and faint line crossed the wide slit. Also, even with a constant-voltage power source there were occasional small electrical instabilities in the recorder circuit, due possibly to electronic and shot noises in the high gain amplifier used. Although these random noises were infrequent and relatively small, they could have been sufficient to mask or make uncertain a small effect such as fine structure maxima.

A fourth factor was the temperature. With the cell employed, there was no means by which the cell could be maintained at any temperature other than that of the surrounding air.

Possibly if provision could be made for using a longer cell of larger bore, cooled to a low temperature; and a more efficient spectrograph or spectrophotometer, fine structure might yet be found.

Extinction Coefficients Graph. Both of the principal contributors to the study of the visible spectrum of ozone, Colange and Vassy, have published tables or graphs of extinction coefficients for the spectrum in this region. However, both have worked only with ozone-oxygen mixtures of uncertain composition at atmospheric pressure and unmeasured intermolecular effect of the oxygen on the ozone, and both obtained their coefficients by use of photographic photometry, which is a difficult technique and subject to many errors. For these reasons it was felt desirable to make a series of measurements on pure ozone under

controlled conditions to verify or refute their findings, which are not in good accord.

In order to obtain as trustworthy a graph of the molar extinction coefficients of ozone in the region under consideration as possible, all the traces of pure ozone made with the recording spectrophotometer were corrected to a common pressure of five centimeters by use of the density-pressure graph for 3300 Angstroms, and an average value was taken for the extinction coefficient at each wavelength. The final graph was constructed from these average values.

Overall, there was good agreement from one trace to another so that the average value graph differs only slightly from any of the individual run graphs. In general the values obtained for this graph agree more closely with those given by Colange than with the values of Vassy, but this is not of much significance, since a change in pressure of the surrounding gas in the cell would produce some change in the absorbing power of the ozone, and both Colange and Vassy worked with dilute mixtures which would be subject to this effect.

In general contour, the curve obtained is intermediate between those of Colange and Vassy. It exhibits several minor maxima, as does Colange's graph, but somewhat displaced from his and not so pronounced. The major maxima observed at 6010, 5770, 5350 and 5050 Angstroms are agreed upon by all three graphs, and their locations might presumably be reasoned to be well known. The minor maxima, however, do not agree so well. The present graph places maxima at 5480, 5200, 4930, 4700 and 4600 Angstroms, which placement should be accurate to within ten Angstroms on either side. Colange places maxima at 5460, 5150, 4900, 4750

tion, increasing it somewhat. To this second group belong argon, oxygen, nitrogen and carbon tetrachloride vapor.

The remaining two gases, carbon dioxide and water vapor fall into the third group. These gases exert a considerably stronger effect on the ozone spectrum than those of the second group. Even at low pressures of about five centimeters or less they cause increase in the extinction coefficients of ozone of about twice the magnitude of the change due to group two gases, even when these are used at two atmospheres pressure. Of these gases, water has a dipole moment of 1.85 Debyes and carbon dioxide has a zero dipole moment, since it is a linear symmetric molecule. It has, however, a considerable quadrupole moment due to the difference in electronegativity of carbon and oxygen. This might be expected by comparison with the carbonyl group in organic compounds, which has a dipole moment of 2.8 Debyes.

This leads to the conclusion that there are two separate forces at work on the ozone molecule due to the foreign gas present. In the second group only one of these is important, namely a pure pressure force which might have the effect of forming a Van der Waals complex with the ozone molecule, due to a Le Chatelier type reaction.

The other, and more interesting group would exert not only this pressure effect, but also a somewhat more powerful effect due apparently to a dipole-dipole or dipole-induced dipole type of interaction between the ozone molecule and the compressant gas molecules, to form a sort of solvated ozone molecule which has apparently much greater absorbing power. This is in agreement with the findings of Robinson in his work

on solutions of ozone in various solvents.

At first glance it would seem that carbon tetrachloride should fall into the second rather than the first group, as carbon dioxide does, since it should have a considerable quadrupole moment. Probably the reason it does not while carbon dioxide does is that with carbon dioxide the molecule is spindle shaped and the central carbon, to which the bonding is apparently attached, is exposed to attack on four sides. Carbon tetrachloride, on the other hand, is a symmetric tetrahedron with the carbon placed at the center and consequently well shielded by chlorine atoms, so that sterically the ozone is prevented from coming within bonding distance of the carbon.

These observations agree qualitatively with the appearance of the spectrum in the visible region. As shown in Table I, the region around 6166 Angstroms corresponds to the amount of energy required to decompose ozone into oxygen atoms in ^3P states and oxygen molecules in $^1\Delta$ states. Now since the ground state of the oxygen molecule is $^3\Sigma$ and for the oxygen atom it is ^3P, by symmetry rules it is necessary that the ground state of the ozone molecule be a $^1A_1$ state, while the $^1\Delta$ and ^3P decomposition corresponds to a $^3A_1$ state, and ordinarily a transition such as this is forbidden on the basis of the necessary change of multiplicity. There is, however, the possibility that in the presence of a strong electric or magnetic field such as would obtain in the vicinity of an oscillating dipole, this rule could be relaxed somewhat. This could be due to the field changing the electronic configuration and hence the wave function for the molecule, so that it would no

longer be strictly in a $^1A_1$ state and could change somewhat into the $^3A_1$ state necessary for the observed energy values. Accordingly, in the pressure effect, the presence of a dipole could make possible the transition to the excited $^3A_1$ state, causing the absorption in the visible region. Qualitatively, the stronger the dipole attraction, the stronger should be the transition, and hence the greater the absorption of light.

In making the various measurements the region at 3300 Angstroms was chosen as a relatively pressure insensitive standard by which to measure the actual amount of ozone present. The sensitivity to foreign gas pressure here is small and this region was used rather than the less sensitive region at 3200 Angstroms because the lines at 3300 are broad and the setting of wavelength and slit are not so critical, whereas the sharp lines at 3200 demand exactly reproducible settings. Although this region is temperature sensitive, the temperature variation throughout the measurements did not exceed a degree or so, and was neglected.

In practice, a graph of density versus pressure was made at 3300 Angstroms, using pure ozone. Then when a pressure dependence run was made, a measurement taken at 3300 for each trace allowed the pressure of ozone to be found by interpolation on the graph. This graph is shown in Figure 12.

In calculating results, the pressures were corrected by means of the pressure-density graph, then the traces were adjusted to make the 6010 maxima coincide on all the traces for a given set of measurements. In general, the change in extinction coefficients was smallest at this

maximum and increased as one measured farther from this peak in either direction.

A table of measured extinction coefficients for various pressures of ozone and foreign gas is given in Table II, showing the small magnitude of the effect at 6100 Angstroms. From this table and the individual graphs may be calculated the extinction coefficients for the various mixtures at the pressures used.

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APPENDIX I

A strong series of apparent absorption maxima were observed when the light source alone was photographed on the plate of the spectrograph and the spectrum densitometered. These maxima could not be due to residual ozone or some unknown gas in the cell since they appeared equally strongly whether the cell was evacuated or left full of air. The spacing was entirely wrong for it to have been a polarization effect. After considerable experimentation, an apparently correct solution was found for the phenomenon. The spectrograph in use was equipped with a replica reflection grating, which consisted of a collodion film bearing the ruled surface, which was cemented to a concave mirror of correct curvature. As the light from the slit passed through the collodion film to the ruled surface and back out, it suffered interference similar to the familiar Newton's rings phenomenon. If we represent the angle of incidence of the light as φ_1 and the angle of reflectance as φ_2, and the thickness of the film as L, then if two rays of light strike the collodion, one of them being reflected from the front surface and the other from the back surface, the excess geometrical path traveled by the rear ray will be

$$\frac{L}{\cos \varphi_1} + \frac{L}{\cos \varphi_2} \doteq 2L$$

The excess optical path will be approximately 2nL, where $n = 1.5$ is the

refractive index of collodion. If k is the order of interference, λ is the wavelength of the light and ν its frequency, then

$$k\lambda_1 = 2nL$$

$$(k-1)\lambda_2 = 2nL$$

Hence

$$1 = k-(k-1)$$

$$= 2nL(1/\lambda_1 - 1/\lambda_2)$$

$$= 2nL\Delta\lambda/\lambda^2$$

$$= 2nL\Delta\nu$$

If $\Delta\nu$ is approximately 1000 centimeters^{-1} and equal to $\Delta\lambda/\lambda^2$

$$1 = 2nL \cdot 1000$$

$$L = 1/3000$$

$$= 3.3 \text{ microns}$$

Then the wavelengths at which reinforcement will occur, causing maxima, will be

$$\lambda(\text{maximum}) = 2nL/k$$

$$= 10 \text{ microns}/k$$

k	λmaximum	λmaximum observed
15	6670 Angstroms	6670 Angstroms
16	6250	6250
17	5890	5890
18	5550	5550
19	5260	5260
20	5000	5000
21	4760	4760
22	4550	4550

These values correspond to within the error of measurement.

APPENDIX II

In order to cancel out the false band structure arising from the interference at the grating, it was thought that a mask mounted in front of the film might be employed. This mask was to be made of a film exposed the proper time and developed. Then the maxima would have exposed this film more strongly and it would be darkest right at the maxima. To compute the correct exposure time, assuming the reciprocity law to hold fairly well, we set up the following computations, in which λ is the wavelength of light, γ is the gamma of the film.

At the slit, the light intensity is $E(\lambda)$
At the film, the light intensity is $E''(\lambda)$
The mask has $T'(\lambda)$ from previous exposure $E'(\lambda)$

Then the characteristics of the Hurter and Driffield curve for the film are

$$\begin{aligned} -\log T &= \gamma(\log E - \log E_o) \\ &= \gamma \log E - C \end{aligned}$$

where E_o is the incident light and E is the transmitted light in photometry of the film. So

$$\begin{aligned} -\log T'(\lambda) &= \gamma(\log E' - \log E_o) \\ &= \gamma \log E' - C \end{aligned}$$

At the film, with the mask in place,

$$\begin{aligned} \log E''(\lambda) &= \log E(\lambda) + \log T'(\lambda) \\ &= \log E(\lambda) + C - \gamma \log E'(\lambda) \end{aligned}$$

And

$$\begin{aligned} -\log T''(\lambda) &= \gamma \log E''(\lambda) - C \\ &= \gamma \log E(\lambda) + \gamma C - \gamma^2 E'(\lambda) - C \\ &= \gamma \log E(\lambda) - \gamma^2 \log E'(\lambda) + (\gamma - 1)C \end{aligned}$$

For - log T" to be constant, hence for the false bands to be exactly suppressed

$$\begin{aligned} \gamma \log E(\lambda) - \gamma^2 \log E'(\lambda) &= 0 \\ \log E(\lambda)/\log E'(\lambda) &= \gamma \end{aligned}$$

Hence

$$\begin{aligned} D &= C(\gamma - 1) \\ &= (\gamma - 1)\log E_o \\ &= - \log T''/T_o \end{aligned}$$

Plotting D as function of log time t and measuring γ as the slope of the curve, then if the customary exposure time t is 30 seconds, the correct exposure time t_1 for the mask is given by

$$\log 30/ \log t_1 = \gamma$$

With the film used, γ was approximately one, so t_1 was about 30 seconds also. In practice, a 9 second exposure was about the best. This would imply that the reciprocity law was not holding too well for our work.

APPENDIX III

The calculations involved in this work were almost exclusively repetitive applications of the Beer-Lambert relations. As an example, assume the following data:

At five centimeters pressure of ozone in a cell 121 centimeters long, the measured intensity of light was found to be 46.8 while that of the light source thru the empty cell was measured as 87, both intensities being on the same arbitrary scale. Then, by Beer's equation,

$$T = I/I_o$$
$$= 40.6\%$$

and

$$D = -\log T$$
$$= \log I_o - \log I$$
$$= .390$$

Now by the relation

$$D = \alpha PL$$

in which P is the pressure in atmospheres and L is the length of the optical path in centimeters, we find

$$\alpha = D/PL$$
$$= 49 \times 10^{-3}$$

in which the units are reciprocal centimeter atmospheres.

APPENDIX IV

TABLES AND GRAPHS

TABLE I: Decomposition Methods and Energies for Ozone

O_2	O	Decomposition States		Energy Change	Ozone States	Wavelength
$^3\Sigma$	^3P	$^3\Sigma$	^3P	1.05	$^1A_1\,^3A_1\,^5A_1$	12000 A
$^1\Delta$	^1D	$^1\Delta$	^3P	2.0	$^3A_1\,^3A_2\,^3B_2$	6166
$^1\Sigma$	^1S	$^1\Sigma$	^3P	2.67	$^3A_1$	4650
		$^3\Sigma$	^1D	3.0	$^3A_1$	4140
		$^1\Delta$	^1D	3.96	$^1A_1\,^1A_2\,^1B_2$	3140
		$^1\Sigma$	^1D	4.62	$^1A_1$	2680
		$^3\Sigma$	^1S	5.22	$^3A_1$	2380
		$^1\Delta$	^1S	6.2	$^1A_1\,^1A_2\,^1B_2$	2000
		$^1\Sigma$	^1S	6.86	$^1A_1$	1810

TABLE II: Extinction Coefficients for Ozone at 6010 Angstroms

Extinction Coefficient	Pressure of Ozone	Pressure of Foreign Gas
49 $cm^{-1}atm^{-1}$	4 cm	-
51	4	79 cm N_2
51	4	155 N_2
49	4.45	-
49	4.45	3.5cm H_2O
49	5	-
48.5	5	8 cm CCl_4
49	5	-
46	5	5 cm O_3
49	5	-
52	5	79 cm A
49	5	-
50	5	79 cm O_2
50.5	5	155 O_2
49	4.45	-
51	4.45	79 cm CO_2

TABLE III: Extinction Coefficients of Ozone in the Visible Region as found by Vassy, Colange and the author.

Wavelength	Vassy	Wilson	Colange
4600 Angstroms	4 $cm^{-1}atm^{-1}$	3.5	2.7
4700	3.7	3.8	2
4800	10	7.8	5
4900	10	8	10.5
5000	19	11.6	14
5100	20.1	15.6	15
5200	24.5	19.1	16.8
5300	34.5	27.8	30.6
5400	38.5	31	29.2
5500	44	35	31.6
5600	52.2	41.6	39
5700	60.5	48.7	43.5
5800	60.2	48.5	43.2
5900	59	48.6	40.6
6000	68.2	54.3	44.5
6100	62.5	49.5	46.5
6200	50	41.7	37.3
6300	44	36.7	35.7

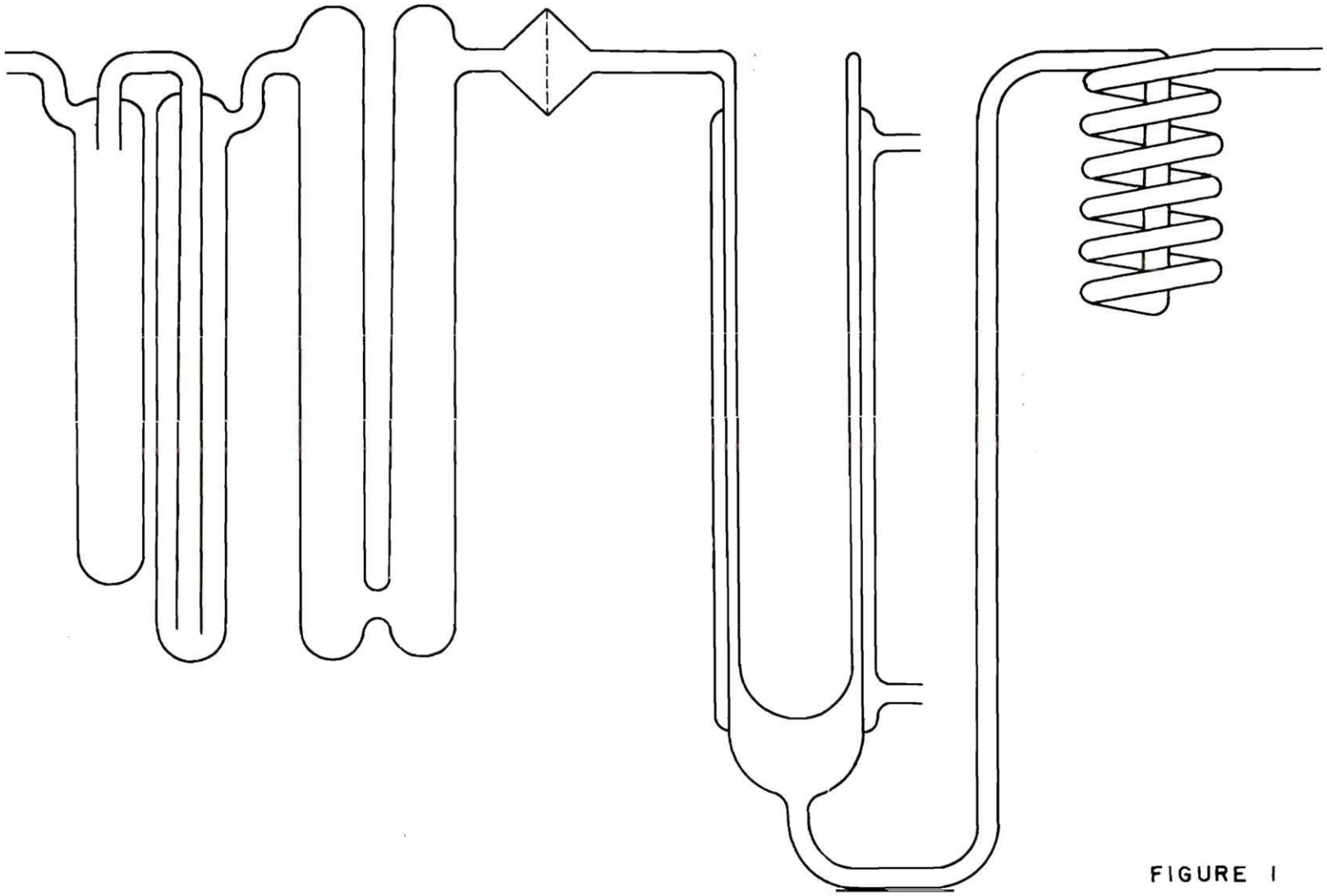


FIGURE 1

OZONIZING TRAIN

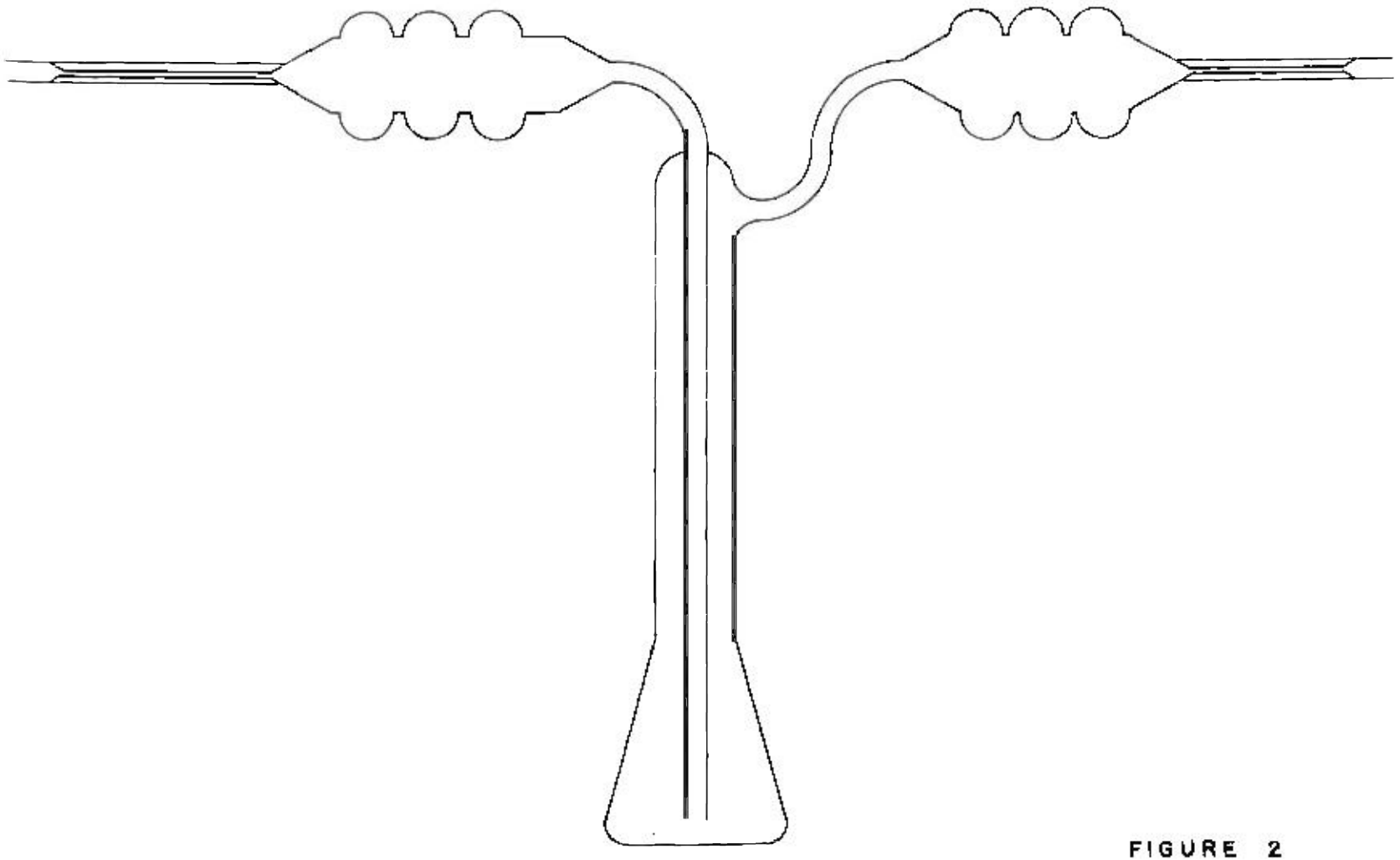


FIGURE 2

CONDENSING CELL

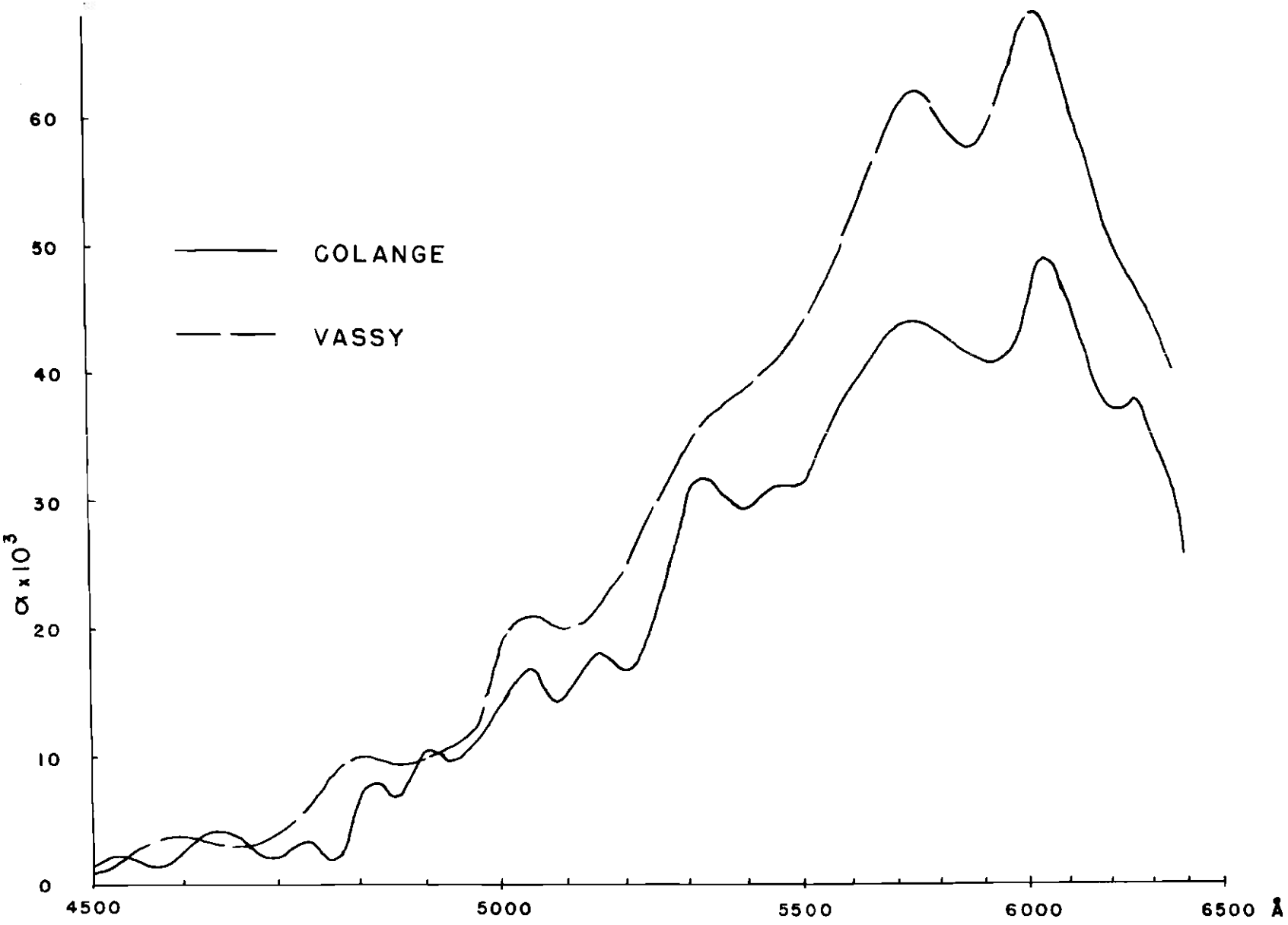


FIG. 3 EXTINCTION COEFFICIENTS FOR OZONE GAS AS OBTAINED BY COLANGE AND VASSY

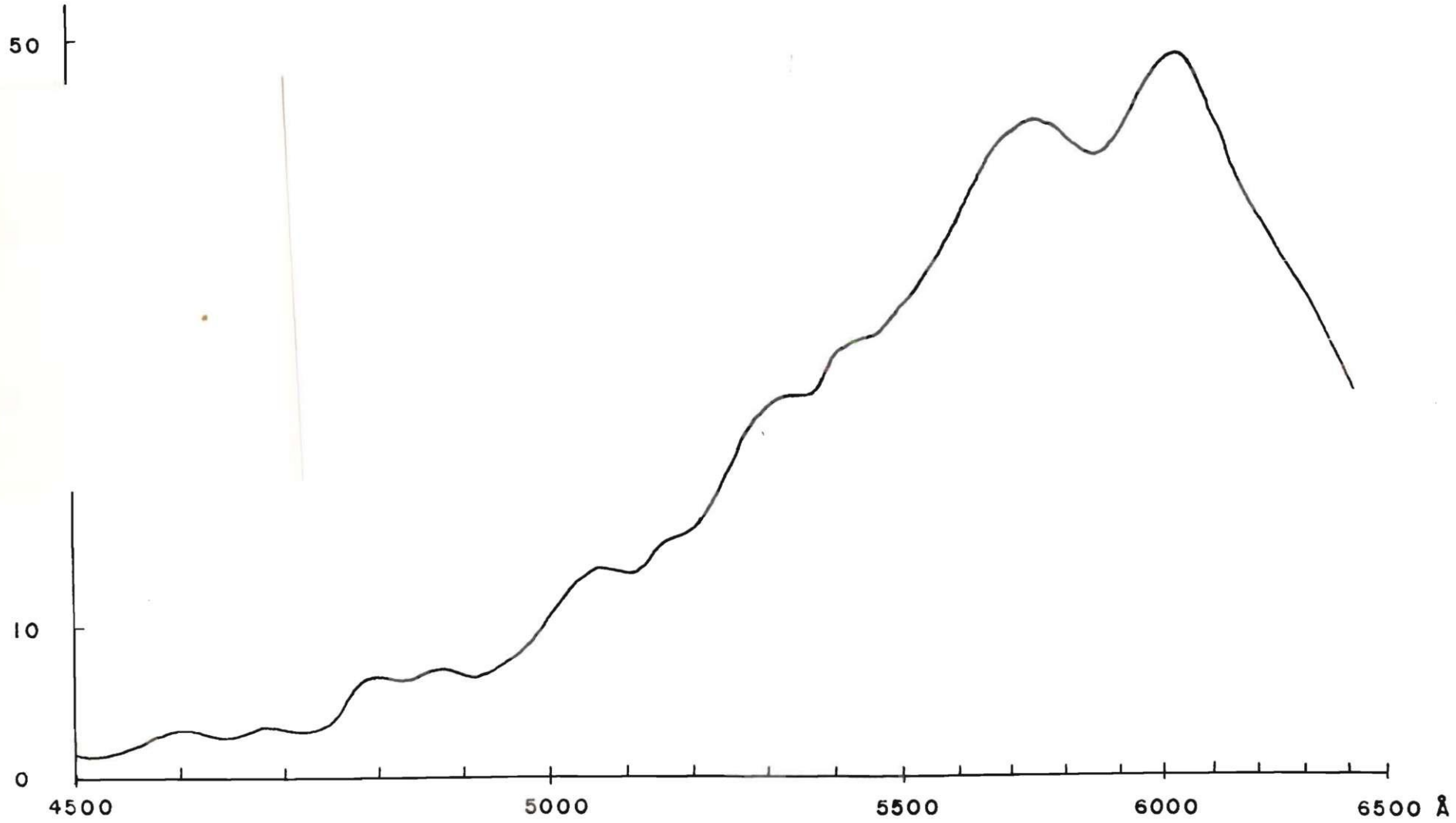


FIG. 4 MOLAR EXTINCTION COEFFICIENTS FOR OZONE GAS AT 5 cm

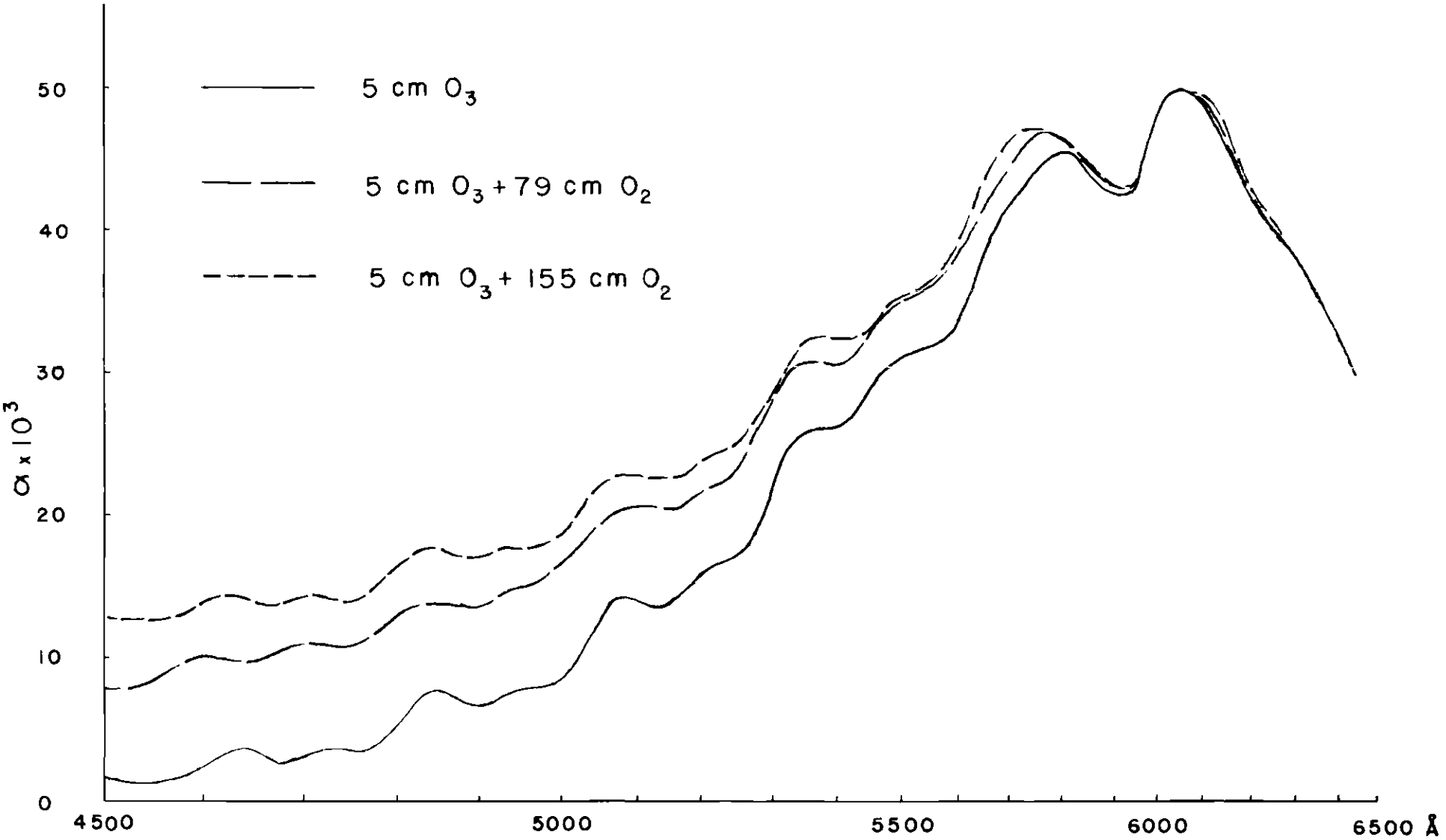


FIG. 5 MOLAR EXTINCTION COEFFICIENTS FOR OZONE – OXYGEN

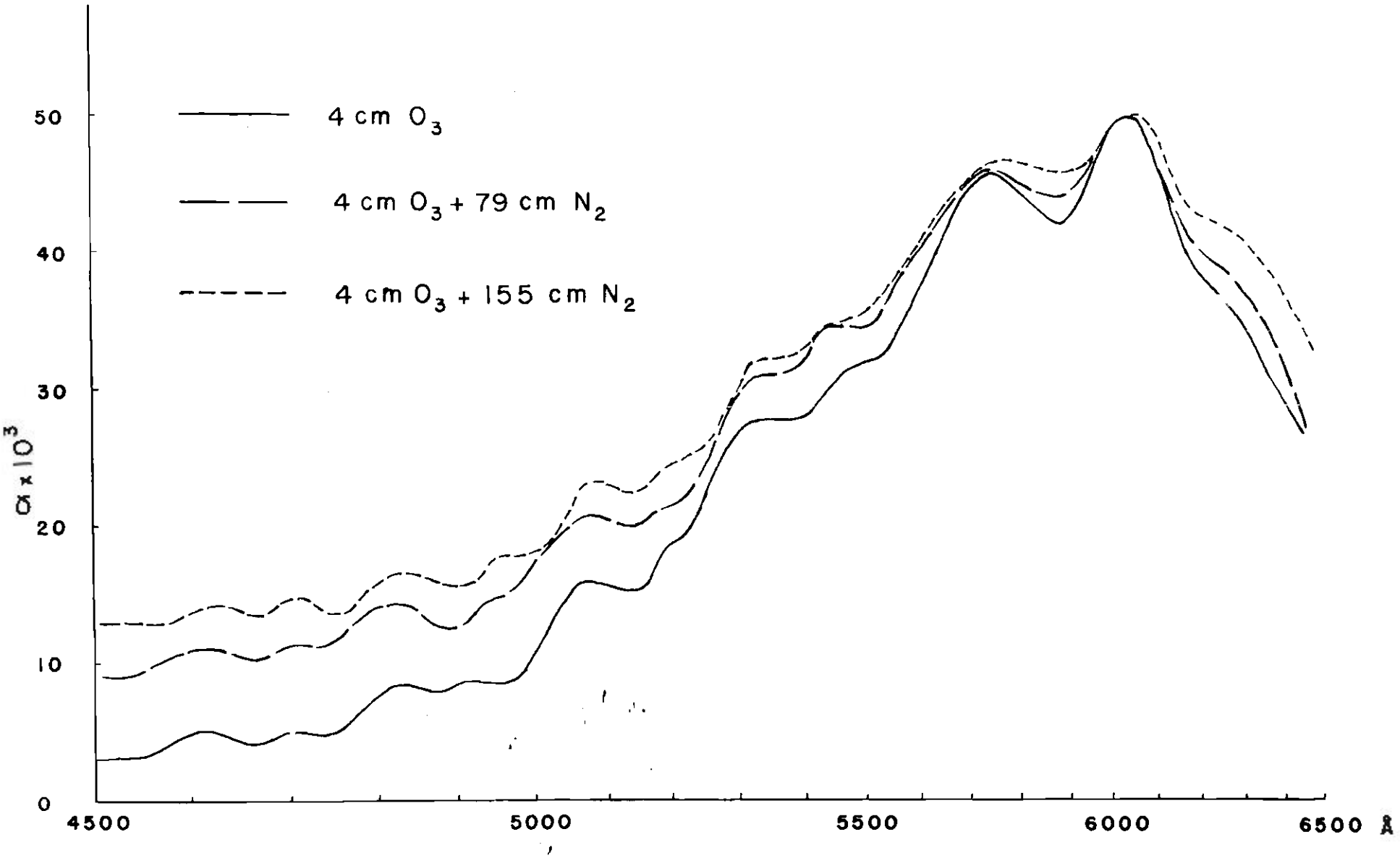


FIG. 6 MOLAR EXTINCTION COEFFICIENTS FOR OZONE — NITROGEN

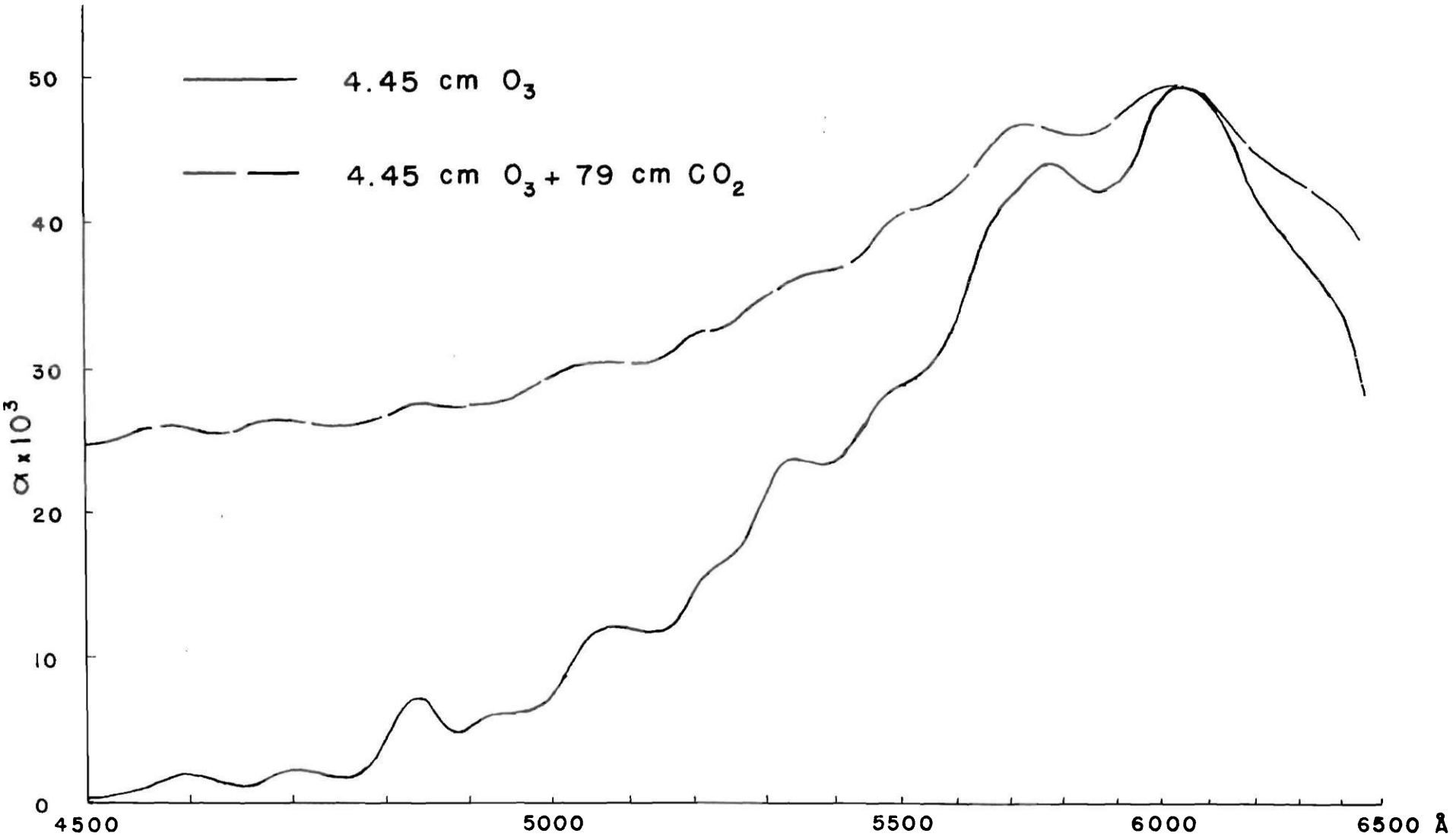


FIG. 7 MOLAR EXTINCTION COEFFICIENTS FOR OZONE — CARBON DIOXIDE

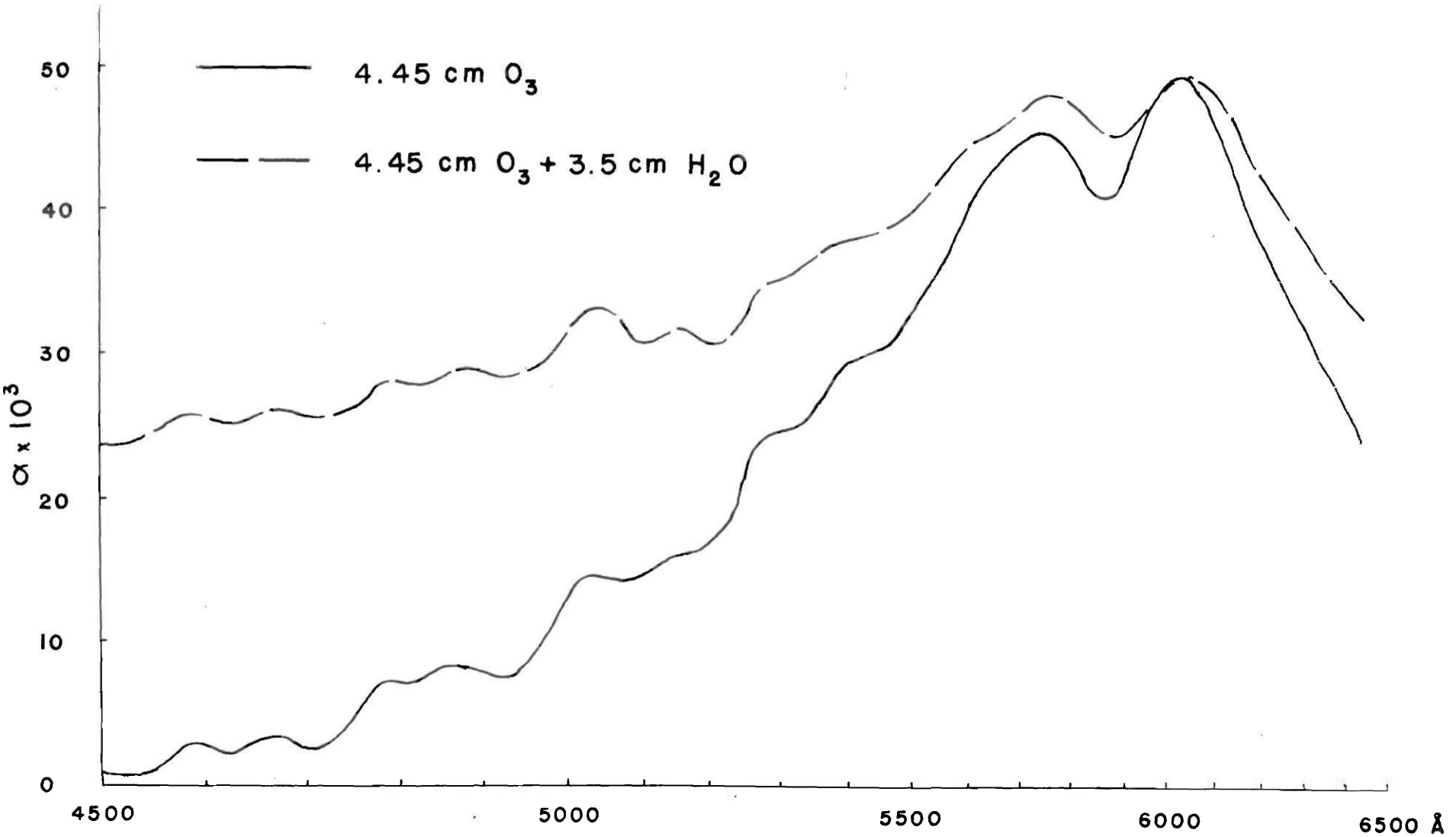


FIG. 8 MOLAR EXTINCTION COEFFICIENTS FOR OZONE – WATER VAPOR

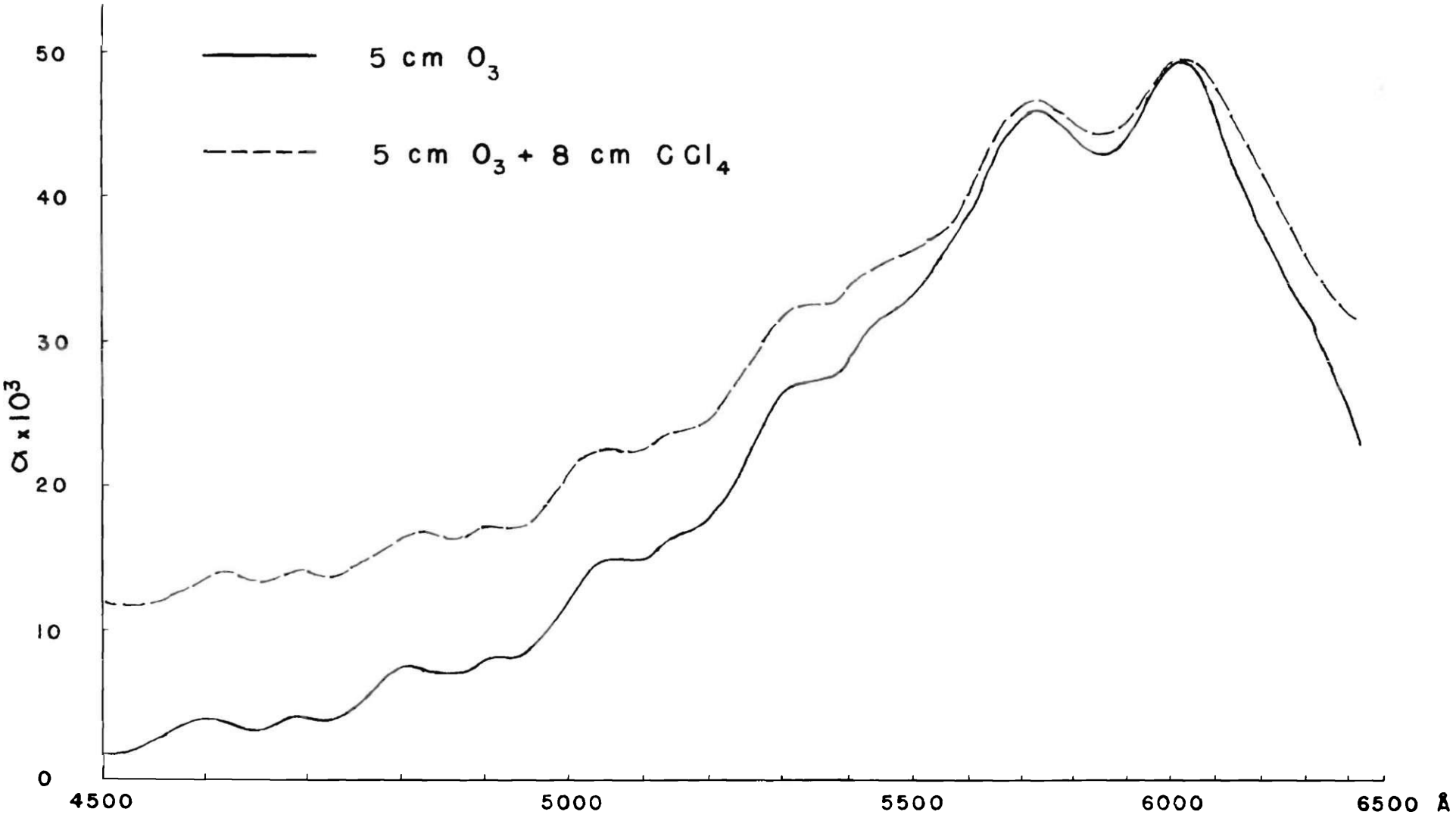


FIG. 9 MOLAR EXTINCTION COEFFICIENTS FOR OZONE - CARBON TETRACHLORIDE VAPOR

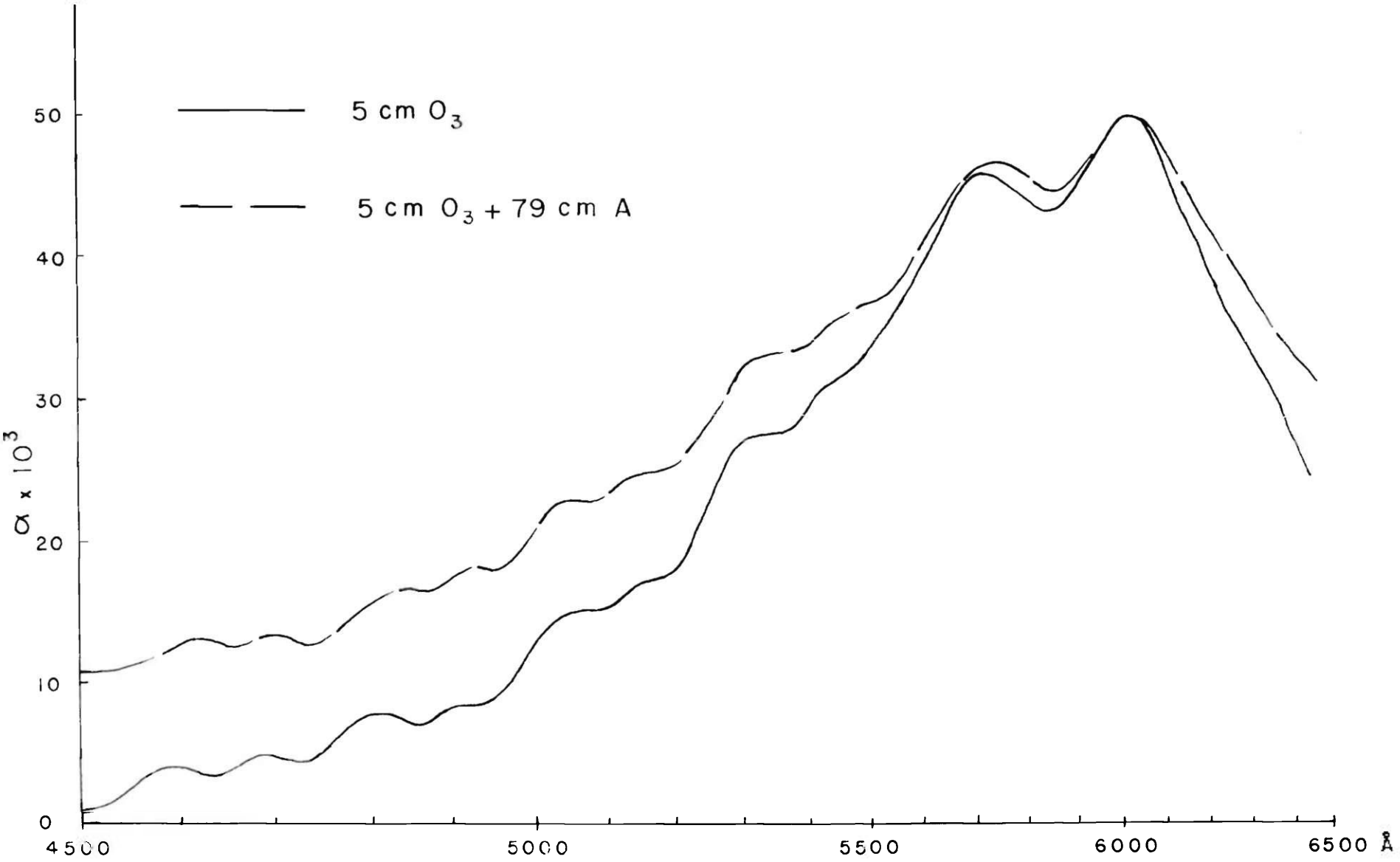


FIG. 10 MOLAR EXTINCTION COEFFICIENTS FOR OZONE — ARGON

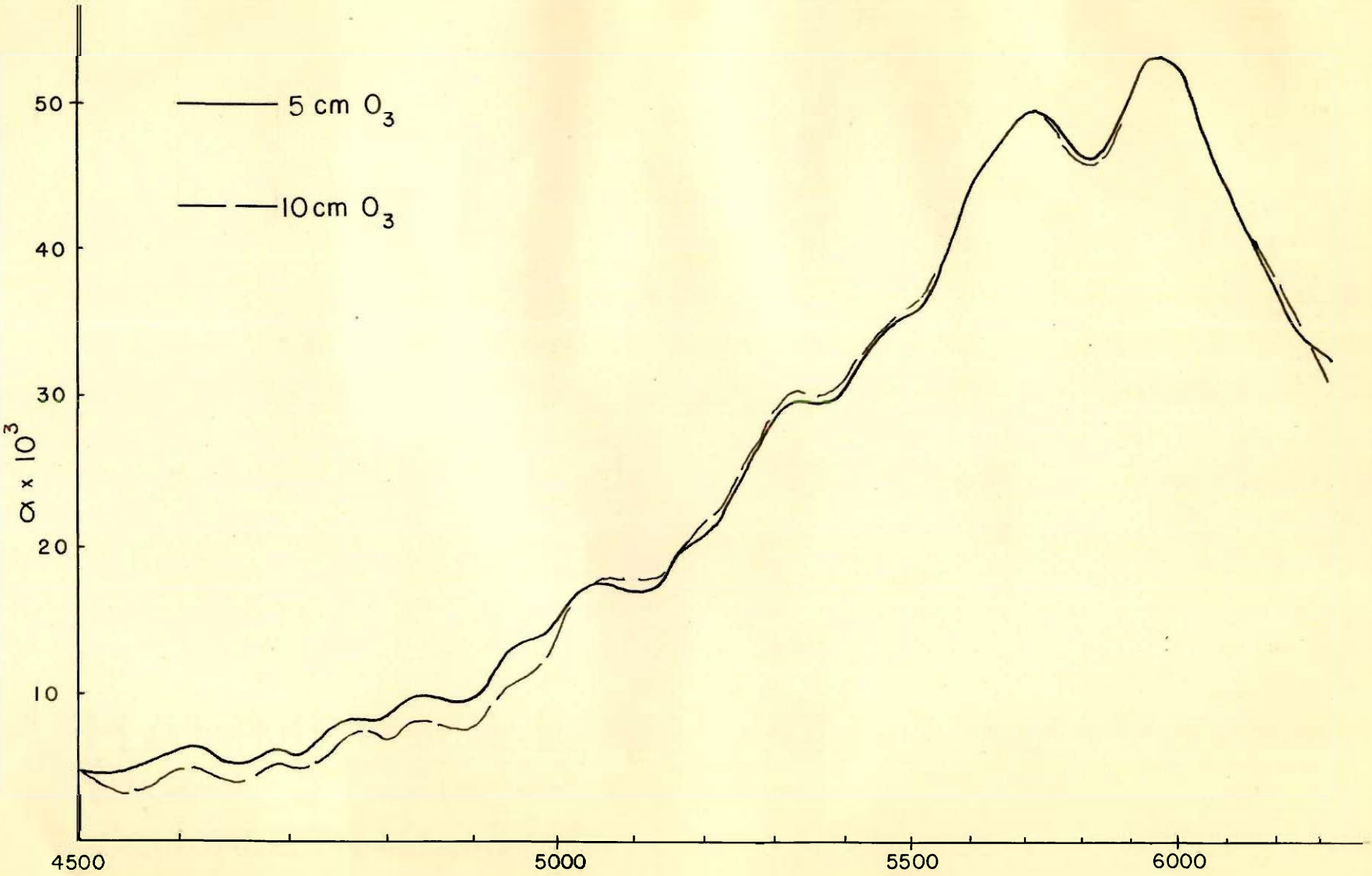


FIG. II MOLAR EXTINCTION COEFFICIENTS FOR OZONE - OZONE

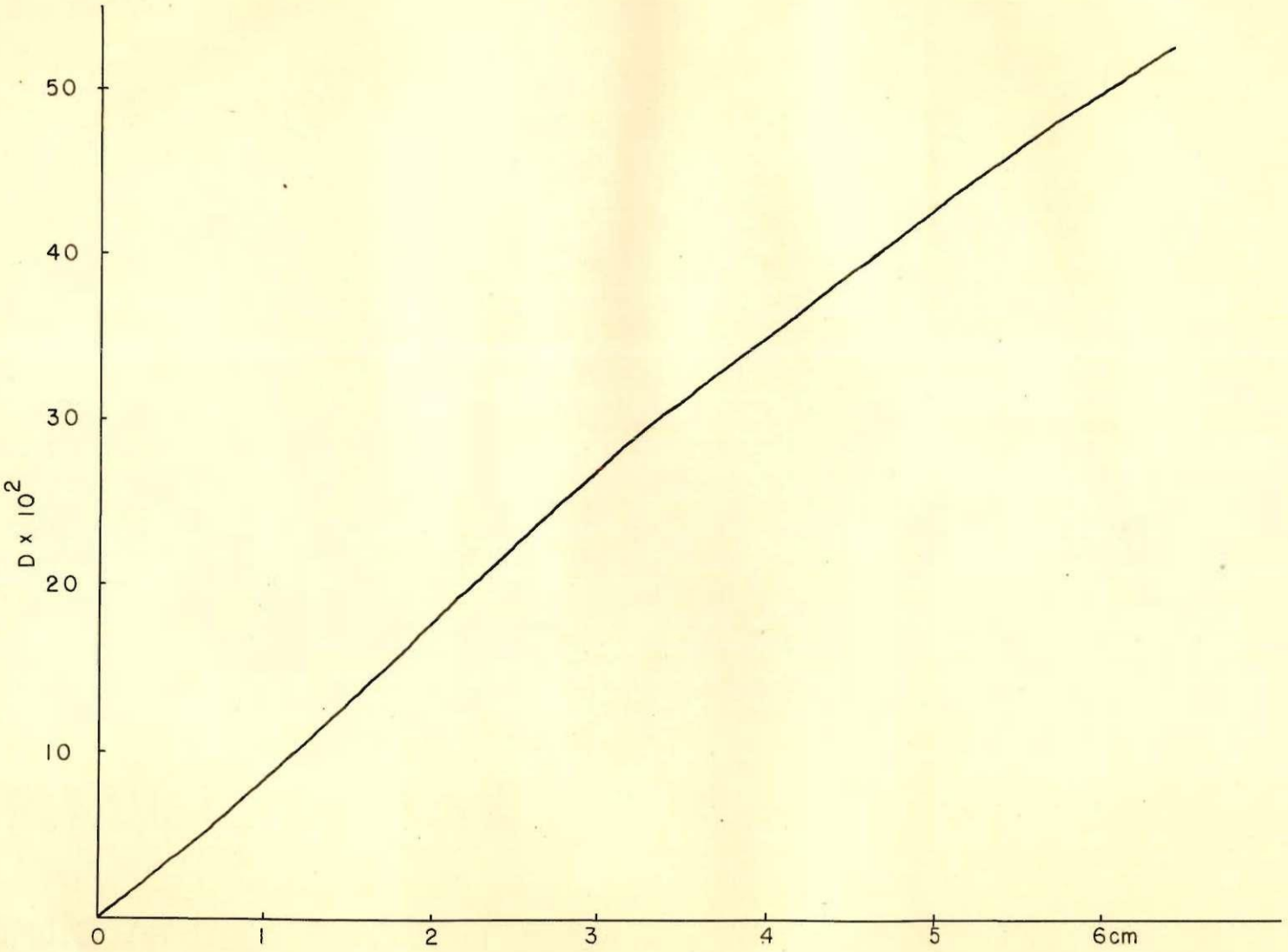


FIG. 12 PRESSURE - OPTICAL DENSITY CURVE FOR OZONE AT 3300 Å

APPENDIX V

PHOTOGRAPHS

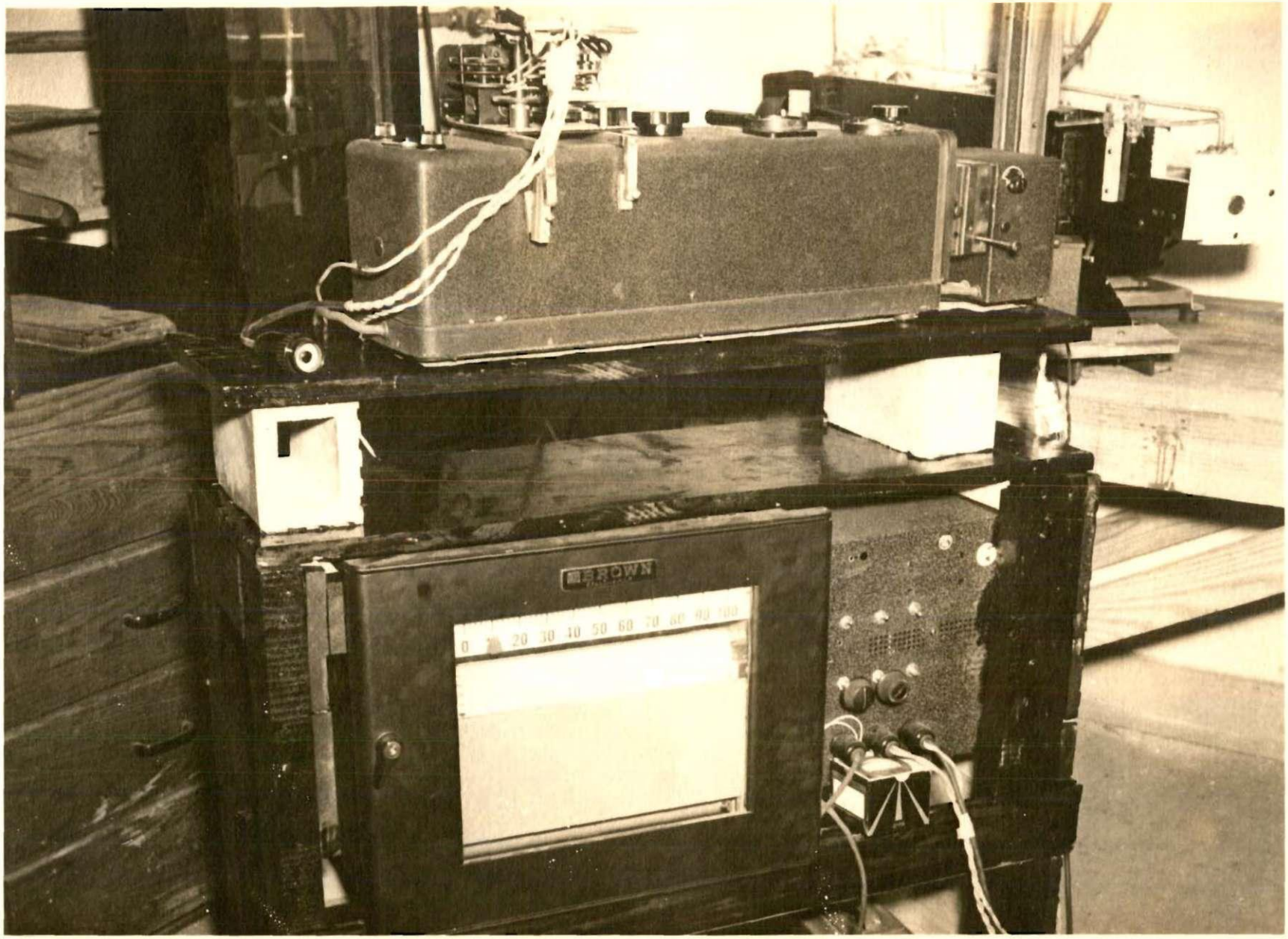


PLATE V RECORDING SPECTROPHOTOMETER

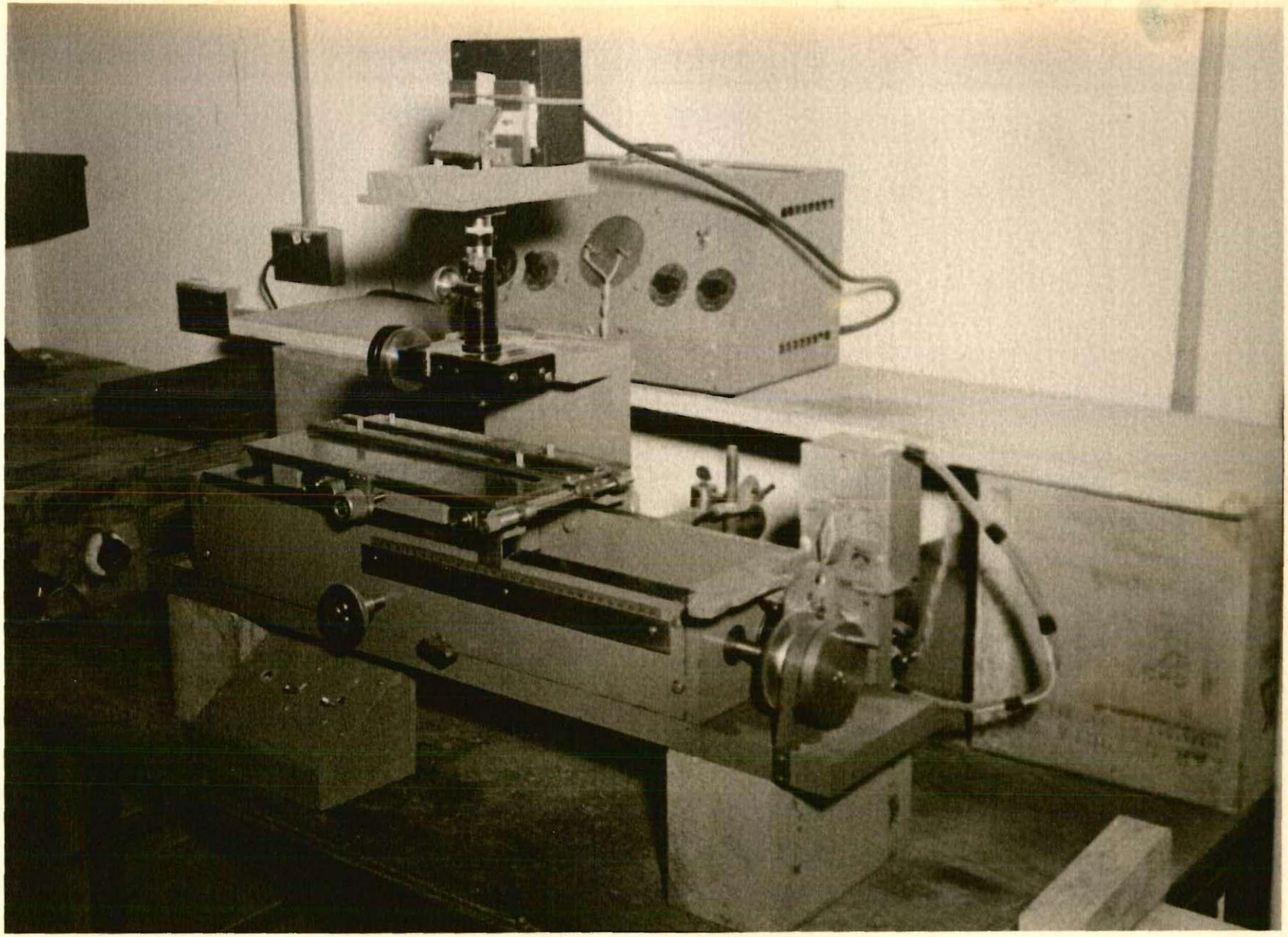


PLATE IV DENSITOMETER

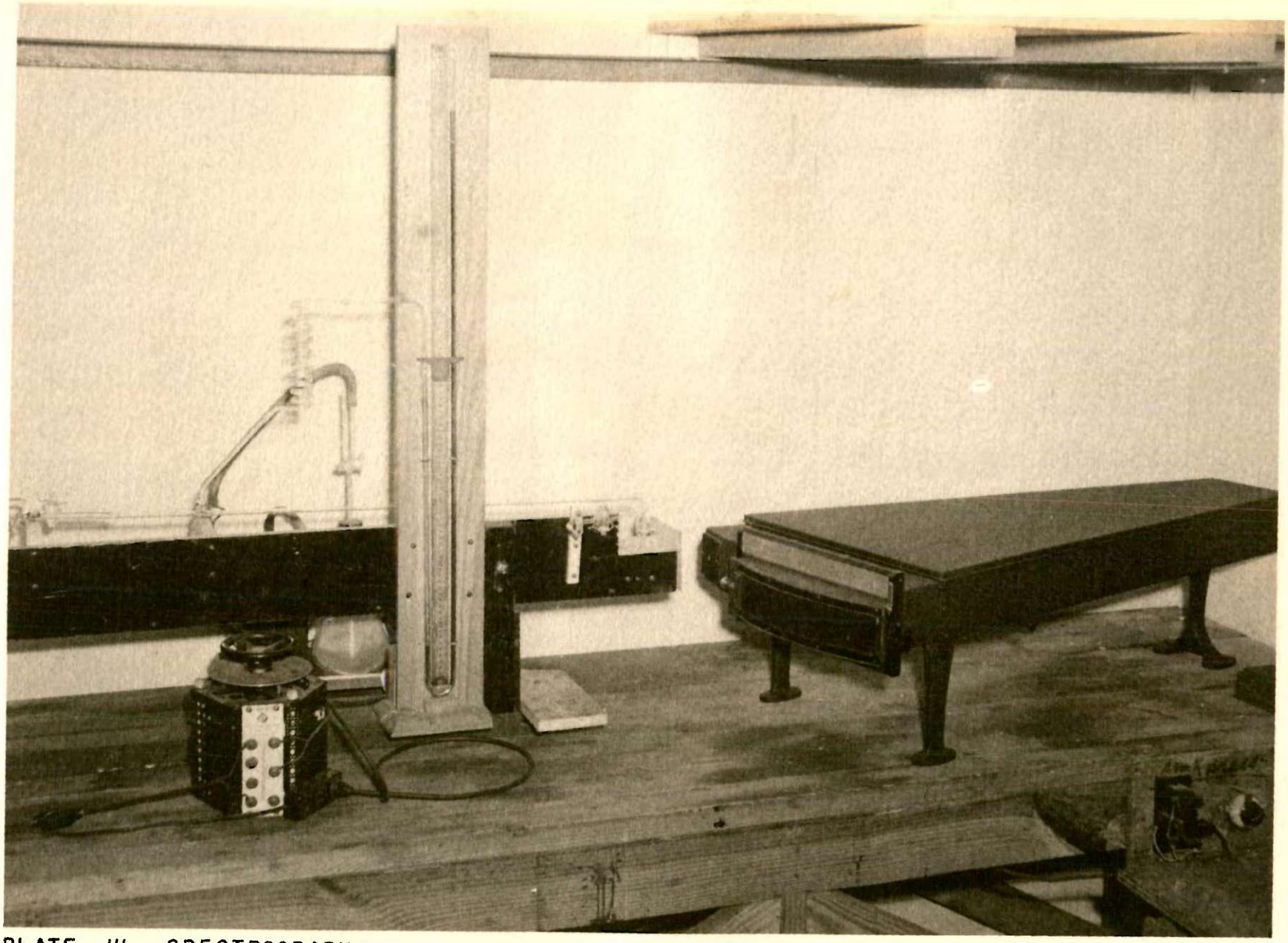


PLATE III SPECTROGRAPH

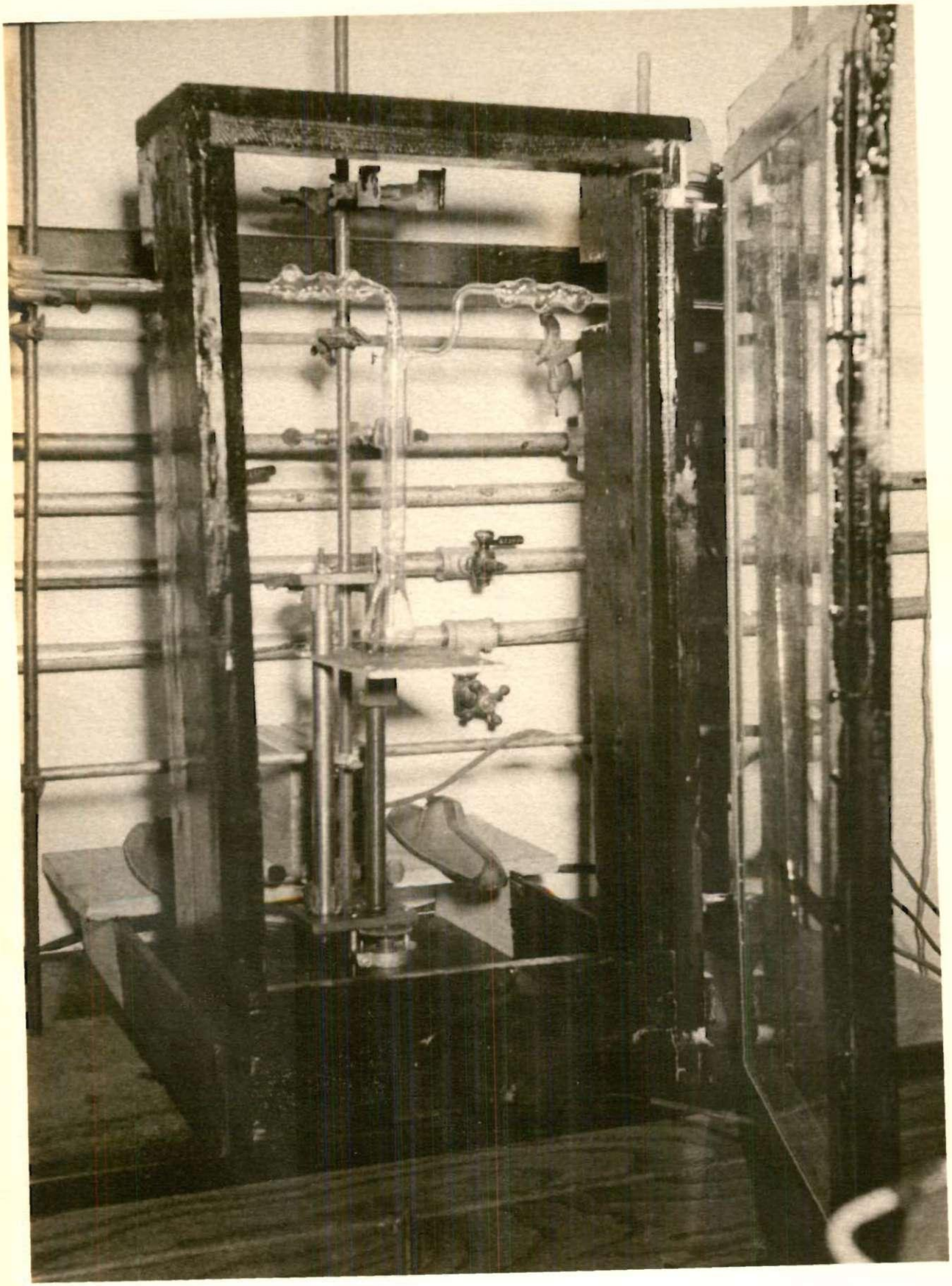


PLATE II CONDENSING CELL

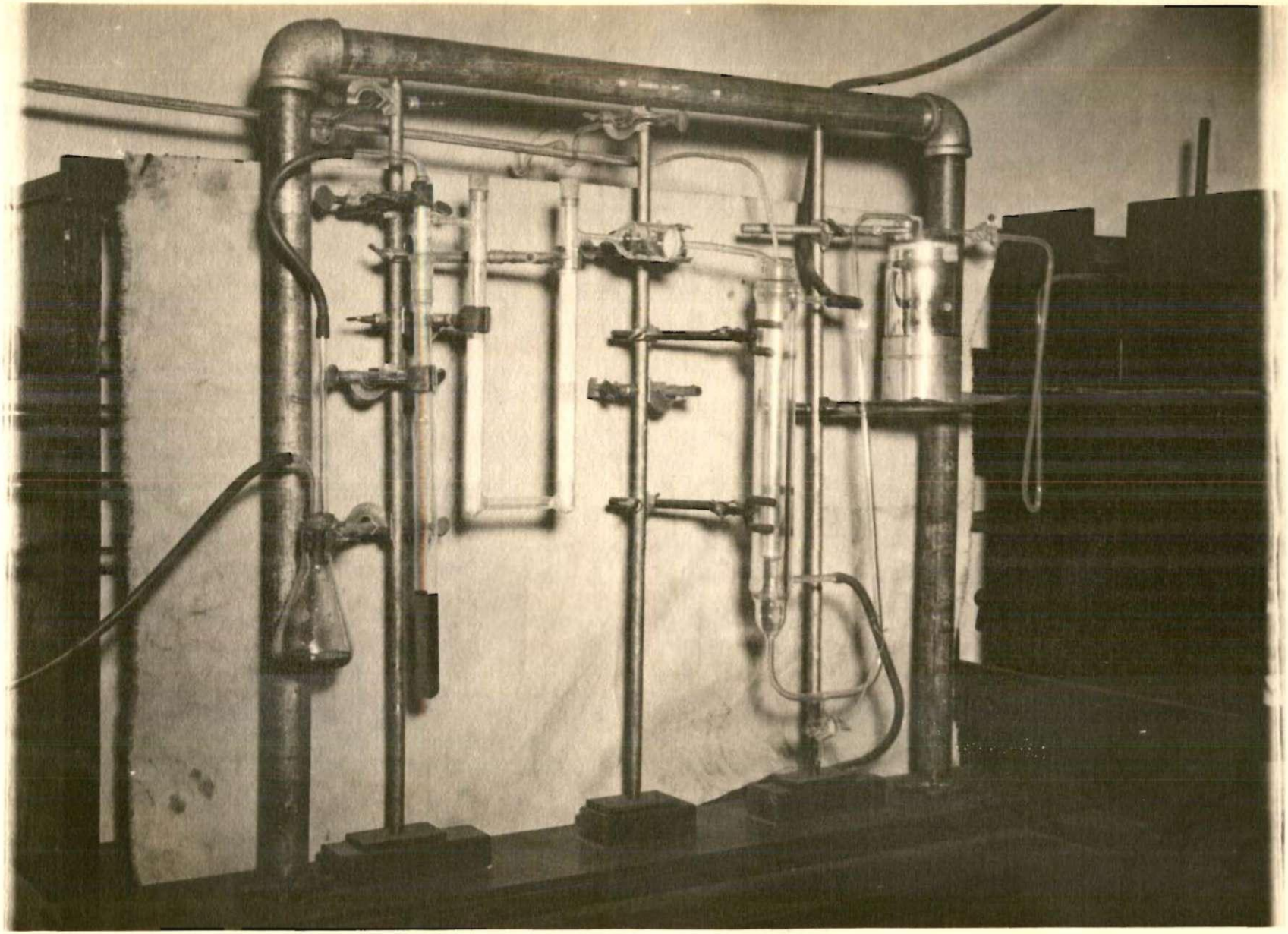


PLATE I OZONIZING TRAIN

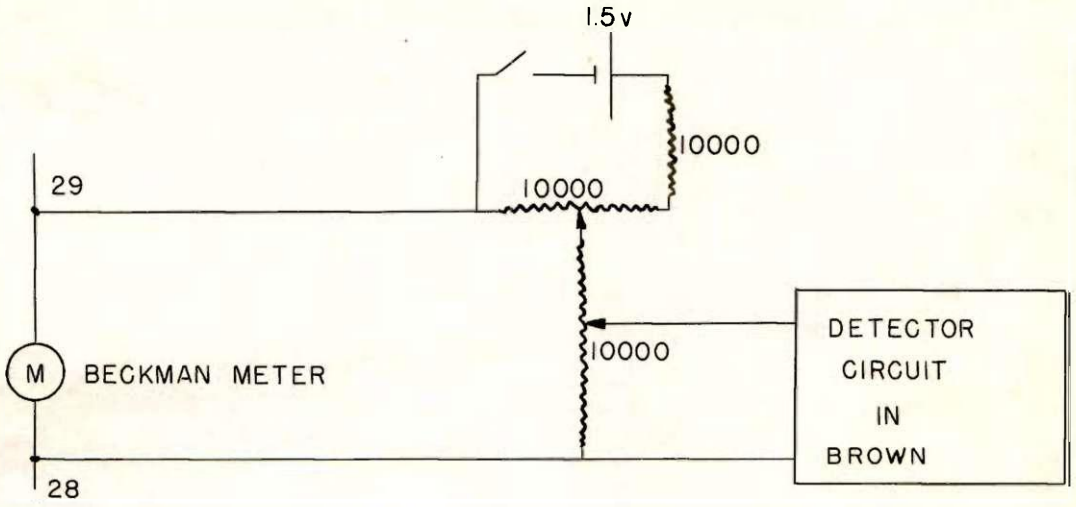
APPENDIX VI

In order to convert the Beckman spectrophotometer, making it recording, it was necessary to add to it a self-balancing follower circuit. In the present case a 25 millivolt Brown Electronik recording potentiometer was available. This instrument contains a detecting circuit which receives the impulse being measured, amplifies it and passes on to a balancing circuit the necessary phase shift to cause the balancing motor to drive in the correct direction.

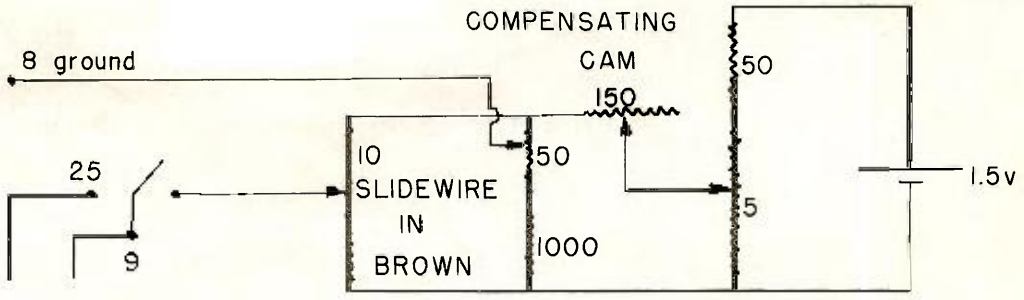
Schematic diagrams of the detecting and balancing circuits as modified for automatic operation are shown in the two appended figures. As shown in the schematic diagram, these two circuits were separated and the voltage across the meter of the Beckman was impressed upon the detector circuit. Since the Beckman potential was about one volt and the range of the potentiometer was only 25 millivolts, a bleeder circuit was connected in to furnish a variable bucking voltage sufficient to cancel the excess voltage. An attenuator potentiometer provided means for adjusting the scale span on the Brown instrument.

To correct for a serious non-linearity in the light intensity

from the light source at different wavelengths, as well as the non-linear response of the photo-cell to light of different wavelengths, a variable resistor was introduced into the balancing circuit. This consisted of a cam mounted on the wavelength drive, the edge of the cam making contact with a radially mounted wire-wound dividohm resistor. As the cam turned, its eccentricity caused its edge to move along the resistor, thus acting as a controlled rheostat. The variation in this resistor introduced or removed sufficient voltage from the balancing circuit to cancel out the non-linearity in the voltage of the light source and photo-cell, when used with no absorbing medium in the optical cell. This made the I_o curve for the machine become almost a straight line with constant position on the recorder regardless of wavelength, where before correction the I_o curve was sharply dependent on wavelength to determine its span.



DETECTOR CIRCUIT



BALANCING CIRCUIT